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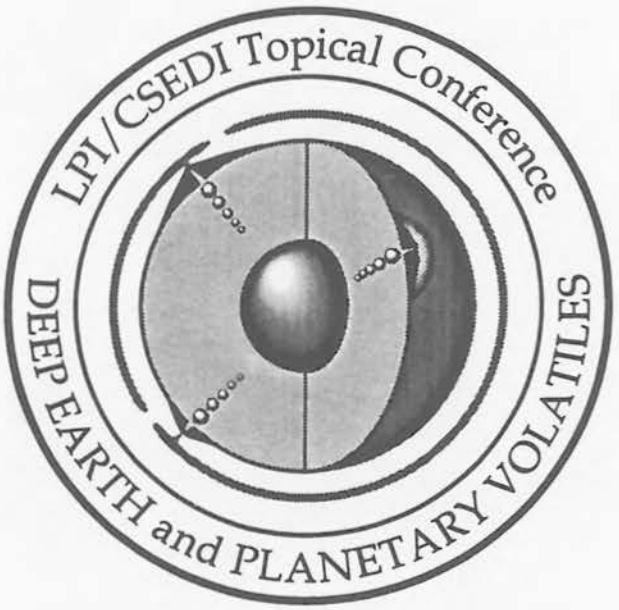

Papers Presented to

Conference on Deep Earth and Planetary Volatiles

September 21–23, 1994
Pasadena, California

PAPERS PRESENTED TO

CONFERENCE ON
DEEP EARTH AND PLANETARY VOLATILES

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Preface

This volume contains papers that have been accepted for presentation at the Conference on Deep Earth and Planetary Volatiles, September 21–23, 1994, in Pasadena, California. The Program Committee consisted of Thomas J. Ahrens *(California Institute of Technology)*, Kenneth Farley *(California Institute of Technology)*, Donald Hunten *(University of Arizona)*, Keith O'Nions *(University of Cambridge)*, Uli Ott *(Max-Planck-Institut für Chemie, Mainz)*, and Kevin Zahnle *(NASA Ames Rearch Center)*.

Logistics and administrative and publications support were provided by the Publications and Program Services Department staff at the Lunar and Planetary Institute.

Contents

Rare gases systematics and mantle structure. C. J. Allègre and T. Staudacher
Laboratoire de Géochimie et Cosmochimie, Institut de Physique du Globe de Paris, Université de Paris VI et VII, 4, Place Jussieu 75252 Paris, France.

About ten years ago we published a general review of rare gases systematic in the atmosphere - mantle - crust system. Our model at that time was self consistent, based on the available data and explained as well helium, as argon and xenon isotopic signatures. It is today certainly not the only possible model, since new data have been obtained and experimental progress was made.

We will emphasize the following points:

— One of the most important ones is certainly the first set of experimental data on the solubility of noble gases in metal phases at intermediate pressures (Matsuda et al., 1993), since the core was certainly not formed at ultra high pressures, as emphasized by Ahrens and confirmed by trace elements systematics Wänke. The experimental data clearly show that the core can not be a major reservoir for terrestrial rare gases.

— The second point is a more elaborate reconsideration of the ^{40}K-^{40}Ar budget of the Earth. This shows that ^{40}Ar contained in continental crust + upper mantle + atmosphere is at maximum half of the ^{40}Ar inventory of the whole earth. This implies the existence of a two layered mantle (Allègre et al., 1994).

— The third point is the discovery by the Australian noble gases group of the existance of high $^{20}Ne/^{22}Ne$ and low $^{21}Ne/^{22}Ne$ isotopic ratios in Loihi seamount samples (ex. Honda et al. 1991, 1993). This results which are different to the MORB ratios (Sarda et al., 1986) confirm the idea of a two layered model, but suggest the existance of a primordial solar type Ne reservoir. Several possibilities about the origin of this ^{20}Ne excess in the mantle will be discussed.

— The high $^{40}Ar/^{36}Ar$, $^{129}Xe/^{130}Xe$ and $^{134}Xe/^{130}Xe$, $^{136}Xe/^{130}Xe$ are confirmed by new data. The corresponding ratios for the lower mantle will be discussed. $^{40}Ar/^{36}Ar$ ratios up to 6000 can be accepted and will not modify the general model of the mantle. They confirm the atmosphere chronology, about 85% of the atmosphere was formed in the first 50 My and 15% later on.

— We will also discuss the results obtained on xenoliths or phenocrysts in different lava types and try to constrain the information they carry, using the simple idea that xenocrysts in hot spots do not derive from the deep source as the magma which carry them.

– Finally we have quantitatively explosed the steady-state upper mantle model and constrains the differents values of the mantle reservoirs.

Allègre C.J., K.O'Nions, and A. Hofmann, 1994, in press.

Matsuda J., Sudo M., Ozima M., Ito K., Ohtaka O. and Ito E., Noble gas partitioning between Metal and Silicate under high pressures, Science 259, 788-790, 1993

Honda M., McDougall I., Patterson D.B., Doulgeris A. and Clague D.A., Possible solar noble gas component in Hawaiian basalts, Nature 349, 149-151, 1991

Honda M., McDougall I., Patterson D.B., Doulgeris A. and Clague D.A., Noble gases in submarine pillow basalt glasses from Loihi and Kilauea, Hawaii: a solar component in the Earth, Geochim. Cosmochim. Acta 57, 859-874, 1993.

Sarda et al. Neon isotopes in submarine basalts, Earth Planet. Sci. Lett., 91, 73-88, 1988.

VOLATILES IN THE EARTH; ALL SHALLOW AND ALL RECYCLED. Don L. Anderson, Seismological Laboratory, California Institute of Technology, Pasadena, CA 91125

A case can be made that accretion of the Earth was a high-temperature process and that the primordial Earth was dry. A radial zone-refining process during accretion may have excluded low-melting point and volatile material, including large-ion lithophile elements toward the surface, leaving a refractory and zoned interior.

Water, sediments and altered hydrous oceanic crust are introduced back into the interior by subduction, a process that may be more efficient today than in the past. Seismic tomography strongly suggests that a large part of the uppermantle is above the solidus, and this implies wet melting. The mantle beneath Archean cratons has very fast seismic velocities and appears to be strong to 150 km or greater. This is consistent with very dry mantle. It is argued that recycling of substantial quantities of water occurs in the shallow mantle but only minor amounts recycle to depths greater than 200 km. Recycling also oxidizes that mantle; ocean island ("hotspot") basalts are intermediate in oxidation state to island-arc and midocean ridge basalts (MORB). T his suggests a deep uncontaminated reservoir for MORB.

Plate tectonics on a dry Earth is discussed in order to focus attention on inconsistencies in current geochemical models of terrestrial evolution and recycling.

IMPACT DEGASSING OF WATER AND NOBLE GASES FROM SILICATES. S. Azuma[1], H. Hiyagon[1], Y. Iijima[2] and Y. Syono[3], [1]Department of Earth and Planetary Physics, University of Tokyo, Tokyo 113, JAPAN, [2]Department of Earth and Planetary Science, Nagoya University, Nagoya 464-01, JAPAN, [3]Institute for Materials Research, Tohoku University, Sendai 980, JAPAN.

Previous shock experiments by Ahrens and his colleagues show that degassing of H_2O and CO_2 occurs at 8–65GPa from hydrous minerals such as serpentine [1,2]. In early solar system, the impact degassing would have played an important part in the formation of primary-atmospheres of the terrestrial planets. However, degassing conditions of noble gases are not well-known because there are few experiments for them [3,4]. We conducted some shock recovery experiments to investigate the degassing condition and to understand the degassing mechanisms of water and noble gases.

We used natural richterites (*Ri*), amphibolites (*Am*), serpentines (*Sep*) and orthoclases (*Or*) as target samples. These, except *Sep*, contain radiogenic noble gases such as ^{40}Ar. The samples were put in stainless steel containers, and were shot by a rail gun at ISAS or single-stage powder guns at Nagoya or Tohoku Univ., Japan. We used two kinds of containers : 'open' type containers having a ventilating path for released volatiles for most of samples and 'closed' type ones for some samples for comparison. On *Ri* and *Sep*, we made shock experiments for pre-heated (at 400–500°C) and unheated targets, and for powdered and uncrushed samples. Water and noble gases were analyzed both for the recovered shocked samples and the unshocked original samples, and the fractions of the degassed volatiles were calculated by comparing them. Water content in the sample was analyzed by thermo-gravimetry. Noble gases were extracted by heating the samples under high vacuum and analyzed with a sector-type mass spectrometer.

The results for impact-induced water loss are shown in Fig.1. Water loss for pre-heated (at 400°) *Sep* was about two times larger than that for unheated *Sep* at pressures of 30–40GPa, but no difference was observed for pre-heated and unheated *Ri* up to 43GPa. X-ray diffraction analyses show that serpentine was not decomposed into olivine + pyroxene by shock, but decomposed into the amorphous structure. The mechanism of water loss from *Sep* is most likely diffusion from the amorphous part, but that from *Ri* may be different. Water loss from the powdered *Sep* is high (30–60%) at 40GPa, but that from the uncrushed *Sep* is relatively low (20%) at the same pressure, which is not consistent with the previous work [1,2].

Degassing of radiogenic noble gases, such as ^{40}Ar, from *Or* and *Am* was observed at shock pressures of 15–68 GPa. Observed degassing of lighter gases (He, Ne) from *Or* seemes consistent with the idea of diffusional loss. However, loss of He was not observed for *Am* even at pressures where loss of radiogenic ^{40}Ar was observed. The degassing mechanism of radiogenic ^{40}Ar seems different from that of trapped noble gases.

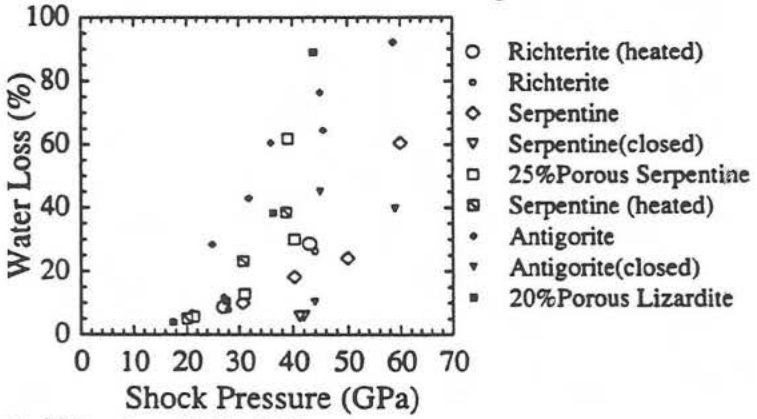

Fig.1 Shock-induced water loss (%) from richterites and serpentines at various shock pressures(GPa). The data of Antigorite and Porous Lizardite are from [1] & [2].

Reference: [1] Lange M.A. et al. (1985)*G.C.A. 49*, 1715–1726. [2] Tyburczy J.A. et al.(1990)*E.P.S.L. 98*, 245–260. [3] Gazis C. and Ahrens T.J.(1991) *E.P.S.L. 104*, 337–349. [4] Ahrens T.J. et al.(1992) *LPSC XXIII*, 3–4 (abstract). [5] Akai J. and Sekine T.(1994)*Proc. NIPR Symp. Antarct. Meteorites*, 7, 101–109.

D/H RATIOS AND H_2O CONTENTS OF MANTLE-DERIVED AMPHIBOLE MEGACRYSTS FROM DISH HILL, CALIFORNIA. David R. Bell and T. C. Hoering, Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., N.W., Washington DC 20015.

D/H ratios are, in principle, useful in characterizing reservoirs of mantle hydrogen and as tracers of volatile transfer processes in Earth's interior. In practice, however, interpretation of isotopic measurements on mantle derived H is complicated by surface processes such as contamination and degassing which may alter the primary D/H ratio. Although there are indications [1-3] that water associated with subduction zones and certain chemically enriched basalts is enriched in D relative to "typical" upper mantle water, the extent of isotopic heterogeneity of mantle H remains uncertain. Kaersutitic amphibole megacrysts in alkaline basalts are one of the most widespread sources of mantle water and are therefore potentially useful for large-scale regional studies of D/H variation. However, D/H ratios of these amphiboles vary widely (from +8 to -113 ‰ [4]), even in samples from the same locality, so that this potential has yet to be realized.

In order to investigate the origin of this variability, and to explore the possibility that primary mantle D/H ratios may be deduced from these amphiboles, we analyzed the D/H ratios and chemical compositions of a suite of 17 kaersutitic amphiboles from Dish Hill, California. This work contrasts with previous studies in which sampling is widespread, but representatives from any given locality are few. Samples were collected from a restricted area on the southern flank of the volcanic center and are associated with the basal volcanic breccia [5]. Fourteen of the samples were large single crystals or crystal fragments (megacrysts, 0.4 to 30 grams), believed to derive from pegmatitic veins crystallized from melts in the mantle. Two were coarse-grained intergrowths of amphibole with olivine and spinel, and one was a thin (2 mm) selvage on a peridotite xenolith.

The samples range in Mg# (=100Mg/(Mg+ Total Fe)) from 55 to 85, with the polymineralic intergrowths having highest Mg#'s. In the megacryst samples, the abundances of all elements analyzed by electron microprobe vary systematically with Mg#, giving reason to expect concomitant behavior in the primary water content of these samples. The polymineralic and selvage samples are displaced from these trends to varying degrees. Our preliminary manometry data (not all samples yet analyzed in duplicate) confirm a general systematic behavior for H: 12 of the 14 megacrysts contain from 0.93 to 1.03 wt.% H_2O and have δD_{SMOW} of -46.8 ± 7.1 ‰ (2σ). Two of the megacrysts are displaced from this trend to significantly lower H_2O contents of 0.59 and 0.04 wt. % respectively. δD of the former sample is -9 ‰, while the latter provided insufficient H for isotopic analysis. The polymineralic and selvage samples have H_2O contents of 1.08 to 1.15 wt. %, with δD from -37 to -45 ‰.

The uniformity of these results suggest that primary H content and isotopic composition is preserved in most of these samples. Low H contents of the two anomalous megacrysts and the high D/H ratio are probably the product of dehydrogenation-oxidation [6,7]. It is likely that this process occurred during transport and eruption, as there are no other indications of unusual chemistry in these samples. The high degree of uniformity observed, relative to similar previous studies, may be due to local volcanology [6]. Within the limits of current uncertainty of the relevant D/H fractionations, the mean "undisturbed" δD of -46 ‰ is consistent with equilibrium with water, occurring as OH groups in a melt, of δD near -70 ‰, typical of depleted upper mantle. The MORB-like affinity of these megacrysts is indicated by their Sr isotope compositions [8].

We conclude that H-isotope information, useful for global systematic studies, can be extracted from mantle-derived kaersutitic amphiboles, providing the appropriate consideration is given to petrology and volcanology of the samples.

References. [1] Poreda, R. 1985 EPSL 73, 244-254. [2] Poreda, R. et al. 1986 EPSL 78, 1-17. [3] Dobson, P.F. and O'Neil, J.R. 1987 EPSL 82, 75-86. [4] Boettcher, A.L. and O'Neil, J.R. 1980 Am.J.Sci 280A 594-621 [5] Wilshire, H.G and Nielson-Pike, J.E. 1986 in GSA Guidebook, Southern California Field Trips 15 (P.L. Ehlig, ed), 9-11. [6] Aoki K. 1963 J. Petrol. 4, 198-210. [7] Dyar, M.D. et al. 1992 Geology 20, 565-568. [8] Basu, A.R. and Murthy, V.R. 1977 Geology 5, 365-368.

THERMOCHEMISTRY OF DENSE HYDROUS MAGNESIUM SILICATES. Kunal Bose[1], Pamela Burnley[2] and Alexandra Navrotsky[1]. [1]Department of Geological and Geophysical Sciences and Center for High Pressure Research, Princeton University, Princeton, New Jersey 08544, USA, [2]Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder, Campus Box 216, Boulder, Colorado 80309, USA.

Recent experimental investigations under mantle conditions have identified a suite of dense hydrous magnesium silicate (DHMS) phases that could be conduits to transport water to at least the 660 km discontinuity via mature, relatively cold, subducting slabs. Water released from successive dehydration of these phases during subduction could be responsible for deep focus earthquakes, mantle metasomatism and a host of other physico-chemical processes central to our understanding of the earth's deep interior.

In order to construct a thermodynamic data base that can delineate and predict the stability ranges of DHMS phases, reliable thermochemical and thermophysical data are required. One of the major obstacles in calorimetric studies of phases synthesized under high pressure conditions has been limitation due to the small (< 5 mg) sample mass. Our refinement of calorimeter techniques now allow precise determination of enthalpies of solution of < 5 mg samples of hydrous magnesium silicates. For example, high temperature solution calorimetry of natural talc ($Mg_{0.99}Fe_{0.01}Si_4O_{10}(OH)_2$), periclase (MgO) and quartz (SiO_2) yield enthalpies of drop solution at 1044 K to be 592.2 (2.2), 52.01 (0.12) and 45.76 (0.4) kJ/mol respectively. The corresponding enthalpy of formation from oxides at 298 K for talc is -5908.2 kJ/mol agreeing within 0.1 % to literature values (Hemingway, 1991[1]: ΔH^{298} (talc) = -5900 kJ/mol).

Approximately 30 mg each of samples Phase A, Phase B, Superhydrous B and Chondrodite have been synthesized for calorimetric and NMR characterization (Burnley et al., in prep.). We present enthalpies of formation data (derived from enthalpies of drop solution in molten lead borate) for some of these phases.

Phase equilibria and thermodynamic analysis of talc and antigorite (serpentine) (Bose and Ganguly, 1993[2]) indicate stability limits near 840 °C at 3 GPa and 750 °C at 7 GPa, very near the onset of stability of DHMS phases (Gasparik, 1993[3]). The calorimetric data in conjunction thermophysical properties of these minerals will permit mapping out the sequence of equilibrium reactions responsible for the introduction, release upon dehydration and subsequent recycling of water in the mantle, proximal to a subducting slab.

References: [1] Hemingway, B. R. (1991) *Am. Min., 76,* 1589-1596. [2] Bose, K. and Ganguly, J. (1993) *Geol. Soc. Amer. Abstr. 25,* 213-214. [3] Gasparik, T. (1993) *JGR, 98,* 4287-4299.

MODELING THE EFFECT OF WATER ON MANTLE RHEOLOGY. Ch. Bounama and S. Franck, General Geophysics Group, Potsdam University. P.O. Box 601632, D-14416 Potsdam, Germany.

To study the thermal history of the Earth we use a parameterized model of mantle convection [1]. This model includes a mathematical description of de- and regassing processes of water from the Earth's mantle. The rates of this processes are considered to be directly proportional to the seafloor spreading rate. The kinematic viscosity of the mantle depends on the temperature/pressure as well as on the volatile content. Dissolved volatiles such as water weaken the minerals by reducing their activation energy for solid state creep. Karato and Toriumi [2] showed a power law dependence between creep rate and water fugacity derived from experimental results. Therefore, we use such flow parameters of diffusion creep in olivine under wet and dry conditions to calculate the mantle viscosity as a function of the water content. Because the creep rate is proportional to the concentration of water-related point defects we assume that the water fugacity is proportional to the water weight fraction. An equation for the steady-state strain rate under wet conditions is established. To assess the unknown constant K in this equation, we use flow law parameters given by Karato and Wu [3] as well as the results of McGovern and Schubert [1].

The evolution model is run for 4.6 b.y. Time series of average mantle temperature, volatile loss, mantle viscosity, mantle heat flow, Rayleigh number, and Urey ratio are calculated. The mantle water is outgassed rapidly in less than 200 m.y. The stability of the results against variations of the constant K is tested. With increasing K the influence of water is stronger, the final average mantle temperature is lower. The degassing process is more rapid. Already an increase of K by one magnitude shows an outgassing process of 100 m.y. The final results of the calculated parameters are in the generally accepted range for all numerical simulations.

References: [1] McGovern P. and Schubert G. (1989) EPSL, 96, 27-37. [2] Karato S. and Toriumi M. (1989) Rheology of Solids and of the Earth, Oxford Univ., New York. [3] Karato S. and Wu P. (1993) Science, 260, 771-778.

NOBLE GAS ISOTOPES AND HALOGENS IN VOLATILE-RICH INCLUSIONS IN DIAMONDS. Raymond Burgess and Grenville Turner, Department of Geology, University of Manchester, Manchester, M13 9PL, U.K.

Application of the ^{40}Ar-^{39}Ar method and noble gas studies to diamonds has increased our understanding of their age relationships to the host kimberlite or lamproite [1,2,3] and of the source and composition of volatile-rich fluids in the upper mantle [4,5]. The properties of diamond (inert, high mechanical strength and low gas diffusivities) means they are especially useful samples for studying gases trapped deep within the earth (<150 km) as they are unlikely to have undergone loss or exchange of entrapped material since formation. Volatile-rich fluids (H_2O-CO_2) are important agents for metasomatic processes in the upper mantle, and the noble gases and halogens preferentially partition into this phase leading to a strong geochemical coherence between these groups of elements.

The abundances of the halogens in the major reservoirs of the Earth shows a marked progression from chlorine, concentrated in the oceans, through to iodine which, through its affinity for organic material, is concentrated mainly in sediments. Abundances in the upper mantle are low. This is particularly true for iodine which is of special interest in view in view of its potential significance as an indicator of sediment recycling and by way of its link to ^{129}Xe anomalies in the mantle through the now extinct isotope ^{129}I. Extensions of the ^{40}Ar-^{39}Ar technique enable measurements of halogens and other elements (K, Ca, Ba, U) by production of noble gas isotopes from these species during neutron irradiation. Samples analysed in this way include 15 coated stones from an unknown source in Zaire, 3 boarts from the Jwaneng and 1 boart from the Orapa kimberlites, both in Botswana

Stepped heating of diamonds gives a bimodal release of Ar with peaks at 1200°C and at the graphitisation temperature of 2000°C. Both temperature intervals give high $^{40}Ar/^{36}Ar$ values of 20,000-30,000 typical of the upper mantle value (e.g. MORB). $^{40}Ar^*/Cl$ value are uniform at around 8×10^{-4} molar [4,5] in all stones analysed. Br/Cl shows a narrow range with a mean of $(1.4 \pm 0.3) \times 10^{-3}$ (n=19), mainly within the range of values reported for oceanic basalts and spinel lherzolites ($1.3\text{-}8 \times 10^{-3}$). The iodine content of the stones is highly variable, even between stones from a single locality; some stones contain no iodine, while others only show a single release at either high or low temperature. Similarly, there is a wide variation in I/Cl of $(0.3\text{-}4.6) \times 10^{-5}$ (n=12) which appears to be lower than values reported for other mantle samples ($2\text{-}20 \times 10^{-4}$). These features indicate decoupling of the geochemical behaviour of I from Br and Cl, an explanation of which is being sought through analyses of carbon and xenon isotopes. We estimate that the volatile-rich fluids within the diamonds show a factor of 5,000 or so enrichment of halogens and ^{40}Ar compared to upper mantle values, which we estimate at about 8 ppm Cl, 26 ppb Br and between 0.1-0.9 ppb I.

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ORIGIN AND LOSS OF THE VOLATILES OF THE TERRESTRIAL PLANETS.

T.M. Donahue, Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, MI 48109, USA.

How the terrestrial planets obtained their original endorsement of volatiles and proceeded to lose them selectively is the theme of this paper. Where good and convincing answers to these questions are still not available, the principal issues are becoming better and better understood, and thus many of the decisive measurements and calculations needed to obtain them can be well defined.

In this paper our present inventories of volatiles such as the noble gases, hydrogen compounds and atmophiles such as CO_2, N_2 and O_2 will be presented. Careful attention will be given to isotopic ratios and their significance. Escape processes past and present - blow off impact erosion, thermal and non-thermal loss of neutral and ionic species will be discussed, and the contribution of each to volatile loss assessed. It will be argued that our understanding of these processes is adequate to explain the present level of fractionation of many of the noble gases and their isotopes on all the terrestrial planets. It will also be argued that we are close to understanding loss of hydrogen well enough to assess reasonably the early abundance of water on early Venus and Mars.

STRUCTURE AND STABILITY OF HYDROUS MINERALS AT HIGH PRESSURE. T. S. Duffy, Y. Fei, C. Meade, R. J. Hemley, and H. K. Mao, Geophysical Laboratory and Center for High-Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Road, Washington, DC 20015.

The presence of even small amounts of hydrogen in the Earth's deep interior may have profound effects on mantle melting, rheology, and electrical conductivity. The recent discovery of a large class of high-pressure H-bearing silicates [1] further underscores the potentially important role for hydrous minerals in the Earth's mantle. Hydrogen may also be a significant component of the Earth's core, as has been recently documented by studies of iron hydride at high pressure [2]. In this study, we explore the role of H in crystal structures at high pressure through detailed Raman spectroscopic and x-ray diffraction studies of hydrous minerals compressed in diamond anvil cells.

Brucite, $Mg(OH)_2$, has a simple structure and serves as an analogue for the more complex hydrous silicates. Over the past five years, this material has been studied at high pressure using shock-compression, powder x-ray diffraction, infrared spectroscopy, Raman spectroscopy, and neutron diffraction. In addition, we have recently carried out single-crystal synchrotron x-ray diffraction on $Mg(OH)_2$ and Raman spectroscopy on $Mg(OD)_2$ at elevated pressure. From all these studies, an interesting picture of the crystal chemical behavior of this material at high pressure is beginning to emerge [3]. Some of the primary conclusions are as follows: First, hydrogen bonding is enhanced by the application of pressure. Second, layered minerals which are elastically anisotropic at low pressure may not be so at high pressure. Furthermore, the brucite data place constraints on the effect of hydrogen on seismic velocities and density at very high pressure. Third, the stability of hydrous minerals may be enhanced at high P by subtle structural rearrangements that are difficult to detect using traditional probes and require detailed spectroscopic analyses. Finally, brucite appears to be unique in that it undergoes pressure-induced disordering that is confined solely to the H-containing layers of the structure.

Ongoing studies are focusing on simulating the pressure-temperature conditions within subducting slabs by using resistively-heated diamond anvil cells. Phase transitions and their kinetics are probed *in situ* by Raman spectroscopy and synchrotron x-ray diffraction. This enables detailed study of possible metastable crystalline transitions and pressure-induced amorphization. A hydrogen-bearing phase that might exist under lower mantle conditions (phase D) has been identified [4], but little is known about its stability or structure. Brucite has also been shown to be stable to very high pressure (78 GPa) at 300°C [5]. Current work is therefore directed toward further exploration of the stability of hydrous phases at lower mantle pressures and high temperatures. Experiments of this sort promise to provide significant new constraints on the potential role of hydrous minerals in the Earth's deep interior.

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Recycling of Volatiles at Subduction Zones: Noble Gas Evidence from the Tabar-Lihir-Tanga-Feni Arc of Papua New Guinea

Kenneth Farley, Brent McInnes and Desmond Patterson (Division of Geological and Planetary Sciences, MS 170-25, Caltech, Pasadena, CA 91125 farley@legs.gps.caltech.edu)

Convergent margin processes play an important but poorly understood role in the distribution of terrestrial volatile species. For example, subduction processes filter volatiles from the subducting package, thereby restricting their return to the mantle. In addition, once extracted from the downgoing slab, volatiles become an essential component in the petrogenesis of island arc magmas. The noble gases, with their systematic variation in physical properties and diversity of radiogenic isotopes, should carry a uniquely valuable record of these processes. However, thus far studies of noble gases in arc volcanics have achieved only limited success in this regard.

Subduction-related lavas and geothermal fluids carry $^3He/^4He$ ratios equal to or slightly lower than those found in the depleted upper mantle source of mid-ocean ridge basalts [e.g. 1]. Apparently slab-derived helium (which should have $^3He/^4He$<< MORB) is extensively diluted by MORB-like helium from the mantle wedge, making it difficult to use helium as a tracer of convergent margin processes. Interpretation of the heavier noble gases (Ne-Ar-Kr-Xe) in arc lavas has also proven difficult, because the lavas carry low noble gas concentrations and hence are subject to pervasive atmospheric contamination [2]. The low noble gas concentrations may be a consequence of degassing in the high level magma chambers characteristic of arc stratovolcanos. We have recently initiated a project to better constrain the behavior of volatiles in subduction zones through geochemical studies of the tectonically unusual volcanos of the Tabar-Lihir-Tanga-Feni (TLTF) arc in the Bismarck Archipelago, Papua New Guinea.

The TLTF arc is the product of complex tectonic forces following the collision of the Ontong-Java Plateau with the Manus-Kilinailu trench approximately 10 million years ago. As a consequence of this collision, subduction jumped westward and reversed polarity, and the former forearc region was subjected to extension. TLTF volcanism was produced by decompression melting in response to this rifting. The primitive, highly alkaline, high fO_2 lavas of the TLTF arc reflect an extraordinarily large slab component derived from the metasomatized mantle wedge or possibly from direct melting of the slab itself [3]. We recently collected basalts, ultramafic xenoliths and geothermal gases from the TLTF islands and several recently discovered seamounts in the region [4].

Preliminary analyses of gases trapped in olivine and pyroxene crystals reveal very low $^3He/^4He$ ratios of 0.2 to 3 times the atmospheric ratio (R_A) compared with values of 6-8 R_A in most arc volcanos [1]. The *excess* argon (i.e. corrected for post-eruptive ingrowth of ^{40}Ar) in these crystals has $^{40}Ar/^{36}Ar$ ratios as high as 45,000. The most radiogenic helium and argon ratios were measured in metasomatic diopside megacrysts hosting primary inclusions of a sulfate-carbonate-water-alkali rich glass which has been attributed to melting of seawater-altered basalt [3]. Such radiogenic ratios have not previously been reported in intraoceanic arc lavas. The low $^3He/^4He$ and high $^{40}Ar/^{36}Ar$ ratios in these lavas require that atmospheric noble gases (1 R_A, $^{40}Ar/^{36}Ar$ =295) have been extensively removed earlier in the subduction process, and are not returned to the mantle by subduction. Additional noble gas analyses in progress, in conjunction with other geochemical tracers, will allow us to further constrain the behavior of volatiles in this convergent margin setting.

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MANTLE DEVOLATILIZATION AND RHEOLOGY IN THE FRAMEWORK OF PLANETARY EVOLUTION. S. Franck and Ch. Bounama, General Geophysics Group, Potsdam University, P.O. Box 601632, D-14416 Potsdam, Germany.

We investigate the thermal history of an Earth-like planet with the help of a parameterized mantle convection model including the volatile exchange between mantle and surface reservoirs [1]. The weakening of mantle silicates by dissolved volatiles is described by a functional relationship between creep rate and water fugacity [2]. We use flow law parameters of diffusion creep in olivine under dry and wet conditions. The mantle degassing rate is considered as directly proportional to the seafloor spreading rate, which is also dependent on the mantle heat flow. To calculate the spreading rate, we assume that the heat flow under the mid-ocean ridges is double the average mantle heat flow. The rate of regassing also depends on the seafloor spreading rate as well as on other factors like the efficiency of volatile recycling through island arc volcanism. Both mechanisms (de- and regassing) are coupled self-consistently with the help of the parameterized convection model under implementation of a temperature and volatile-content-dependent mantle viscosity.

We calculate time series for the Earth's evolution over 4.6 b.y. for the average mantle temperature, the mantle heat flow, the mantle viscosity, the Rayleigh number, the Urey ratio, and the volatile loss. The mantle water is outgassed rapidly within a timescale of less than 200 m.y. for all numerical simulations. The present-day values of the calculated parameters are in the generally accepted range.

In the case of Venus, there is the possibility that the venusian mantle convection might have changed from oscillatory to quasisteady circulation, i.e., Venus changed from an Earth-like planet to a Mars-like planet at around 500 m.y. ago as far as its tectonic style is concerned [3]. Based on this view we also discuss the importance of our model for the investigation of the degassing history of Venus.

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SPATIAL VARIATION OF PRIMORDIAL 3-HE IN CRUSTAL FLUIDS ALONG THE EAST-AFRICAN RIFT SYSTEM

(- the Ethiopian and the Kenya Rift Section -)

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$^3He/^4He$ compositions are presented for groundwater samples from the Ethiopian segment of the East-Afrikan Rift and from its northern extension, the adjacent Afar region (Djibuti). Helium isotope data are compared to those obtained previously from the Gregory Rift, south of Ethiopia. The distribution pattern of mantle-derived volatiles along the entire East-African-Rift (-from south Kenya to Djibuti-) is discussed and their sources are identified.

Helium isotope ratios (R) for samples from the Ethiopian part of the Rift range from 6.3 to 16.0 times the atmospheric ratio ($Ra=1.4 \times 10^{-6}$) and thus show together with a MOR component a considerable hotspot helium component. These mantle helium concentrations are comparable to those observed in groundwaters and volcanic rocks from the Afar plume region in Djibuti. Here R/Ra values range from 9 to 13 times the atmospheric composition, with mantle-derived helium concentrations being higher than at spreading ocean ridges. R/Ra values from Ethiopia and Djibuti are entirely different from those observed in groundwaters at the southerly extending Gregory Rift in Kenya, where R/Ra values scatter between 0.5 and 6. At the northernmost part of the Gregory Rift, close to Ethiopia mantle helium contents are slightly higher, with R/Ra-values varying between 6.5 and 8.0.

The distribution pattern of primordial helium along the East-African-Rift shows an increase in mantle helium contents from south to north, culminating at present at the central rift zone in Ethiopia and at the Afar region in Djibuti. Thus, the obtained helium isotope data clearly demonstrate that, in contrast to other major rift zones, volatiles in groundwaters that issue at the East-African-Rift derive from three distinct sources regions: a crustal, a MOR and a hotspot source. Whereas crustal helium is the principal component in the southern part of the East-African-Rift, along its northern segment it is almost negligiable. Here MOR and hotspot sources are prevailing. The transition zone between a MOR and an OIB source can be located between Lake Turkana in Kenya and the southen edge of the Lakes District in Ethiopia. The observed geochemical observations are in good agreement with seismotectonic and magmatic models along the East-African-Rift.

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TRANSPORTATION OF VOLATILE ELEMENTS IN THERMALLY EVOLVING PLANETESIMALS—AN IMPORTANT ROLE OF METALLIC IRON. K. Hashizume (1), N. Sugiura (2), (1) Department of Earth and Space Sciences, Faculty of Science, Osaka University, Toyonaka, Osaka 560, JAPAN, (2) Department of Earth and Planetary Physics, Faculty of Science, University of Tokyo, Tokyo 113, Japan.

Ordinary chondrites are considered to have experienced thermal metamorphism in small bodies. We are interested in behaviors of volatile elements in such a kind of thermally evolving planetesimals. Volatile elements generally have high vapor pressures at high temperature. In porous bodies, with a high gas permeability, volatile elements are transported efficiently over a long range. Behavior of volatile elements transported by permeable gas flow can be handled by an equation whose form is similar to that of the equation of thermal diffusion. We can follow transportation of heats and volatile elements in planetesimals, when parameters in these equations, initial conditions and chemical behavior of volatile elements are given [1].

Recently, we discovered that nitrogen in equilibrated H-chondrites is mainly trapped in taenite (f.c.c. Fe-Ni), probably dissolved in interstitial sites [2, 3]. Fegley [4] suggests that metallic iron cannot trap nitrogen in the solar nebular gas due to its very low nitrogen partial pressure. Approximately 1 bar of nitrogen pressure is required to explain the nitrogen content in taenite. We may expect high nitrogen gas partial pressure (possibly produced by vaporization of nitrogen-bearing solids such as organic materials) at the interior of thermally evolving planetesimals. Kinetic behavior of nitrogen in taenite suggests that it can easily be equilibrated with the ambient nitrogen gas at temperatures of approximately 500C or higher. We consider that nitrogen is trapped in taenite through a nitrogen redistribution process occurred during the thermal metamorphic event.

Nitrogen-taenite system cannot be closed until it cools down below 500C. Taenite cannot trap nitrogen if nitrogen gas is totally expelled from the interior of the planetesimals during the metamorphic event. Therefore, efficiency of gas transportation is a key parameter to understand the whole story. We present results of our newly improved numerical simulations on gas and heat transportation in planetesimals, and discuss what kind of constraints we can impose on thermal models and accretion models (initial distribution of volatile elements) of chondrite parent bodies. We show that presence of metallic Fe-Ni may have significant influence on transportation efficiency of major atmophile elements such as nitrogen and carbon.

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HYDROGEN AND RELATED MATERIALS AT HIGH DENSITY: PHYSICS, CHEMISTRY AND PLANETARY IMPLICATIONS.

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Recent studies of low-Z molecular materials including hydrogen to multimegabar pressures (<300 GPa) have uncovered a range of phenomena [1] relevant to understanding the nature of the interiors of the outer planets and their satellites. Synchrotron x-ray diffraction measurements (to 42 GPa) have been used to determine the crystal structure of the solid (hexagonal-close packed) and equation of state [1]. Sound velocities in fluid and solid hydrogen (to 24 GPa) have been inverted to obtain elastic constants and aggregate bulk and shear moduli [2]. In addition, an improved intermolecular potential has been determined which fits both static and shock-wave data. Use of the new potential for the molecular envelope of Jupiter suggests the need for major revisions of existing Jovian models or a reanalysis of reported free oscillations for the planet.

Studies at higher pressures (>100 GPa) reveal a sequence of pressure-induced symmetry-breaking transitions in molecular hydrogen, giving rise to three high-pressure phases (I, II, and III). Phase I is the rotationally disordered hcp phase which persists from low pressure to well above 100 GPa at high temperature (*e.g.*, 300 K). Phase II is a low-temperature, high-pressure phase (transition at 110 GPa and 77 K in H_2) with spectral features indicative of partial rotational ordering and crystallographic distortion [1]. The transition to Phase III at 150 GPa is accompanied by a weakening of the molecular bond, gradual changes in orientational ordering, strong enhancement of the infrared intramolecular vibrational absorption, and strong intermolecular interactions similar to those of ambient-pressure network solids. Studies of the phase diagram reveal a triple point near 130 K and 160 GPa [1]. Higher pressure measurements of vibrational spectra place a lower bound of ~250 GPa on the predicted transition pressure for dissociation of molecular hydrogen to form a monatomic metal.

Other low-Z materials, such as H_2O [4], have been studied under static compression above 100 GPa. Novel molecular compounds have been observed over a range of pressures. Studies of H_2-H_2O mixtures reveal a new class of dense clathrates, one of which consists of two interlocking diamond structures in a 1:1 stoichiometry which is stable to at least 30 GPa. Solid compounds involving inert gases have also been observed, first with $He(N_2)_{11}$ [5] and subsequently with $NeHe_2$ and $Ar(H_2)_2$ [6]. These results illustrate that chemical association of normally inert or immiscible components can occur under moderate pressure conditions such as those which prevail in molecular and icy layers of the outer planets and their satellites.

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LOSS OF SOLAR HE AND NE FROM IDPS IN SUBDUCTING SEDIMENT: DIFFUSION AND THE EFFECT OF PHASE CHANGES. H. Hiyagon, Department of Earth and Planetary Physics, University of Tokyo, Tokyo 113, Japan.

The results of the diffusion experiment for solar He and Ne in IDPs in a magnetic separate from Pacific Ocean sediment suggest that solar He and Ne would be easily released from IDP grains and hence lost from subducting slabs at shallow depths [1]. However, since the diffusion experiment was conducted under high vacuum, there may be a possibility that magnetite grains, which are supposedly the main constituent of the magnetic fraction, might be partly reduced to form a metal phase due to low oxygen fugacity in the experimental condition [2]. If this is the case, such a phase change might affect the gas release and hence the results of the diffusion coefficients.

In order to examine whether or not such a phase change really occured in the condition of the diffusion experiment, I conducted a heating experiment for a magnetic separate from Pacific Ocean sediment in the same condition as in the diffusion experiment, and the run products were examined with an X-ray diffraction method. Three samples were prepared; they were wrapped with platinum foil, put in a vacuum line, and heated in a molybdenum crucible for two hours at 500C, 800C, and 950C, respectively. After cooling the furnace, the samples were taken out from the crucible and analyzed with an X-ray diffraction method.

The results of the X-ray diffraction analysis show that magnetite is one of the major constituents of all the heated and unheated samples. The unheated sample also seems to contain maghemite (gamma phase of Fe_2O_3), which has the same crystal structure as magnetite except 1/9 of its cation sites are vacancies. No significant changes were observed in the X-ray diffraction spectra; no peaks of FeO nor Fe were observed. This suggests that magnetite stayed magnetite as a major component of the samples throughout the heating (diffusion) experiment. Only a conversion of some maghemite into magnetite at low temperatures is suggested, though this would not cause serious gas release because essentially no changes in the crystal structure. I speculate that the magnetite was self-buffered inside the platinum foil during the short heating duration in the diffusion experiments.

From the above observation, I conclude that the release of solar noble gases from IDPs in my previous diffusion experiment was mostly due to diffusion, and phase changes of magnetite, if present, would have only a minor contribution to the gas release. It should be noted that an X-ray diffraction analysis provides only qualitative information and hence a small amount of phase changes cannot be ruled out completely. However, this would not affect the conclusion, anyway.

The present study further support the reliability of the diffusion data and hence support the conclusion that solar He and Ne would be lost from subducting slabs at shallow depths.

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SOLAR HELIUM AND NEON IN THE EARTH. M. HONDA[1], I. McDOUGALL[1], and D. B. PATTERSON[1, 2], [1]Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia, [2]Division of Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.

Neon isotopic compositions in mantle-derived samples commonly are enriched in ^{20}Ne and ^{21}Ne relative to ^{22}Ne compared with atmospheric neon ($^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios in atmospheric neon are 9.8 and 0.029, respectively), together with significant primordial ^{3}He. Such results have been obtained on MORBs, intraplate plume-related oceanic island basalts, backarc basin basalts, mantle xenoliths, ancient diamonds and CO_2 well gases [e.g., 1 - 8]. The highest $^{20}Ne/^{22}Ne$ ratio observed in MORB glasses (= 13.6 ± 1.3 [6]) is close to the solar value (= 13.6, as observed in solar wind [9]).

In order to explain the enrichment of ^{20}Ne and ^{21}Ne relative to atmospheric neon for samples derived from the mantle, it is necessary to postulate the presence of at least two distinct non-atmospheric components. The two most likely candidates are solar and nucleogenic [$(^{20}Ne/^{22}Ne)_{solar}$ = 13.6, $(^{21}Ne/^{22}Ne)_{solar}$ = 0.032 [9], $(^{20}Ne/^{22}Ne)_{nucleogenic}$ = 2.5, and $(^{21}Ne/^{22}Ne)_{nucleogenic}$ = 32 [10]]. This is because solar neon is the only known component with a $^{20}Ne/^{22}Ne$ ratio greater than both the atmospheric value and that observed in samples derived from the mantle. Nucleogenic neon is well known to elevate $^{21}Ne/^{22}Ne$ ratios. Neon isotopic signatures observed in mantle-derived samples can be accounted for by mixing of the three neon end members: solar, nucleogenic and atmospheric.

We suggest, therefore, that mantle neon comprises a mixture of a primordial solar component together with variable (time-integrated) amounts of nucleogenic neon. Solar neon and nucleogenic neon in mantle-derived samples are strongly correlated with observed primordial ^{3}He and radiogenic ^{4}He. This reinforces the view that the mantle contains a significant primordial component of solar composition.

The atmospheric component observed in mantle-derived samples appears to be dominantly secondary; this may be derived by interaction between ascending magma and downward percolating seawater or by addition of seawater-derived volatiles to the mantle source region of the magmas from the downgoing subducted slab [e.g., 11, 12].

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ATMOSPHERES OF THE MOON AND MERCURY [1]. D. M. Hunten, Lunar and Planetary Laboratory, The University of Arizona, Tucson, AZ 85721, USA.

Mercury and the Moon have long been considered to be similar objects, but this view was based on limited information at visible wavelengths. It is now known that real differences exist in the atmospheres and in the rock types as deduced from mid-infrared observations. Lunar Ar and perhaps Ne were observed from Apollo landed experiments in spite of a large local background. An ultraviolet spectrometer (UVS) in orbit placed upper limits on a number of gases including H and O. At Mercury, the UVS on Mariner 10 measured H, He, and perhaps O and again a number of upper limits for other gases. Less than a decade ago, emissions of Na and K were observed from the ground, with abundances 2 orders of magnitude smaller on the Moon than on Mercury. It is likely that impacting meteoroids bring a significant amount of water to Mercury, whose atmosphere should therefore contain water vapor. This notion is supported by the recent discovery of radar-bright polar deposits almost certainly composed of ice. A variety of origins is likely for the different components. Impact of meteoroids could supply water, Na, and K, and could also vaporize surface material; Na, K, and Ar could be degassed from the crust. H is probably from the solar wind, and He could reasonably come from degassing or the solar wind. A substantial loss process for all components is photoionization (or dissociation); ions on one side are swept away into the solar wind and on the other are swept back to the surface. This process is complicated at Mercury by its permanent magnetic field, but there is little doubt that both loss and recycling still occur. Some of the recycling probably occurs by way of the magnetotail through nightside auroral precipitation; atoms implanted in the surface will diffuse back into the atmosphere shortly after dawn, an effect that seems to be present for K. Finally the light atoms H and He have high enough velocities to escape directly, an effect that may be enhanced by the suprathermal velocity distributions that are likely to be present.

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PRIMITIVE Xe IN THE ATMOSPHERES OF EARTH AND MARS. G. Igarashi, Department of Earth and Planetary Sciences, Faculty of Science, Hiroshima University, Kagamiyama 1-3, Higashi-Hiroshima 724, Japan.

Published data on Xe isotope compositions in primitive carbonaceous meteorites are examined using multidimentional correlation analysis. Distribution of the Xe data in multidimentional data space, except for ^{129}Xe, can be characterized by a single component, whose isotope composition is identical to "H+L-Xe"[1]. Additional small contributions to the data variations, less than 1% of total variations, can be attributed to "S-Xe"[2] as well as atmospheric contamination.

Isotopic composition of primitive Xe common to the Earth's atmosphere and carbonaceous meteorites are determined with the same assumption as adopted by Pepin and Phinney [1]: primitive Xe is precisely related to fission-free Xe in the Earth's atmosphere by mass fractionation. The determined isotopic composition of primitive Xe is closer to Solar-type Xe [3-6], rather than U-Xe [1] (and the primitive Xe estimated from chondrite-achondrite correlation [7]). Hence, the present published data on Xe isotope compositions in meteorites do not seem to require any special component for the primitive Xe common to the Earth's atmosphere and carbonaceous meteorites. Thus Earth's accreting planetesimals would have trapped Xe from the surrounding nebula gases where Xe isotope composition is identical to Solar-type Xe. The trapped Xe was subsequently subject to isotopic fractionation due to gravitational separation [8,9] as planetesimals grew. Finally fissiogenic Xe from ^{244}Pu was added to form the present Xe isotope composition of the Earth's atmosphere. The amount of fissiogenic ^{136}Xe is estimated to be 2.6% of the total amount of ^{136}Xe in the atmosphere, which is about a half of that estimated by Pepin and Phinney [1] (4.65%).

The same procedure can be done for determining primitive Xe in the Martian atmosphere, with an assumption that primitive Martian Xe is precisely related to fission-free Xe in the Martian atmosphere by mass fractionation. The primitive Martian Xe is not necessarily the same as the primitive Xe in the Earth's atmosphere. In fact, by using SPB (Shergotite Parent Body) Xe [10] as a representative of the Martian atmospheric Xe, we obtain the isotopic composition of primitive Martian Xe very close to Q-Xe [11] and AVCC-Xe [1, 12]. Thus Mars accreting planetesimals would have trapped Xe with an isotopic composition similar to "trapped component" in primitive meteorites. Although the isotopic composition of the primitive Martian Xe is distinctly different from that of primitive Xe in the Earth's atmosphere, the primitive Martian Xe was also subject to isotopic fractionation to almost the same degree as the Earth's atmosphere. The amount of fissiogenic ^{136}Xe is estimated to be 2.3% of the total amount of ^{136}Xe in the Martian atmosphere.

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MARS ATMOSPHERIC LOSS AND ISOTOPIC FRACTIONATION BY PICK-UP-ION SPUTTERING AND PHOTOCHEMICAL ESCAPE. B.M. Jakosky (1), R.O. Pepin (2), R.E. Johnson (3), and J.L. Fox (4). (1) Laboratory for Atmospheric and Space Physics and Dept. of Geological Sciences, Univ. of Colorado, Boulder, CO 80309. (2) School of Physics and Astronomy, Univ. of Minnesota, Minneapolis, MN 55455. (3) Engineering Physics, School of Engineering and Applied Science, Univ. of Virginia, Charlottesville, VA 22903. (4) Institute for Terrestrial and Planetary Atmospheres, State Univ. of New York, Stony Brook, NY 11794.

We examine the effects of loss of constituents of the martian atmosphere due to sputtering by solar-wind pick-up ions and photochemical escape during the last 3.8 billion years. Sputtering is capable of efficiently removing species from the upper atmosphere to space, including the light noble gases; nitrogen and oxygen are removed by both sputtering and photochemical processes. Due to diffusive separation (by mass) above the homopause, removal from the top of the atmosphere will fractionate the isotopes of each species, with the lighter isotope being preferentially lost. This allows current measurements of the isotopic ratios to be used as a measure of the atmospheric evolution as integrated over geologic time.

For carbon and oxygen, isotopic fractionation is buffered by exchange of atmospheric species with non-atmospheric reservoirs of CO_2 and H_2O. This allows us to determine the size of the non-atmospheric reservoirs which are capable of mixing with the atmosphere; these reservoirs can be CO_2 adsorbed in the regolith and/or H_2O in the polar ice caps. Such an exchangeable reservoir is required in order to keep the fractionation of the atmospheric gases as low as is observed.

We have constructed both simple analytical models and time-dependent models of the loss of volatiles from and supply to the martian atmosphere. Both argon and neon require continued replenishment from outgassing over geologic time. For argon, sputtering loss of 0.5-0.9 of the total outgassed argon explains the fractionation of $^{36}Ar/^{38}Ar$ without requiring a distinct epoch of hydrodynamic escape (although the fractionation of Xe isotopes still requires very early hydrodynamic loss). ^{40}Ar also is removed by this mechanism, so that its atmospheric abundance cannot be used to infer the outgassing history without correction for the fraction which has been removed. For neon, the timescale for removal of the present atmospheric inventory is 10^8-10^9 years, and the current ratio of $^{22}Ne/^{20}Ne$ represents a balance between loss to space and continued resupply from the interior; the similarity to the terrestrial value is coincidence. For nitrogen, the loss by both sputtering and photochemical escape would produce a fractionation of $^{15}N/^{14}N$ larger than is observed; an early, thicker carbon dioxide atmosphere could mitigate the nitrogen loss and produce the observed fractionation, as could continued outgassing of juvenile nitrogen.

Based on scaling from the isotopic constraints, the total amount of carbon dioxide lost over geologic time by sputtering is probably of order tens of millibars rather than a substantial fraction of a bar. The total loss from pick-up-ion sputtering and photochemical escape, therefore, does not seem able to explain the loss of a putative thick, early atmosphere that could have been responsible for the crater degradation and valley networks on the oldest geologic units. If these features were formed in the presence of a CO_2 greenhouse atmosphere, the CO_2 must reside currently either in the regolith as extensive carbonate deposits or in the polar caps as ice or clathrate.

THE PRIMARY CARBON AND THE FORMATION OF CARBON SPECIES IN TERRESTRIAL MAGMAS. A.Kadik, V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry,Russian Academy of Sciences, Kosigin St.19, 117975 Moscow, Russia

PROBLEMS. There is general agreement that primary carbon and redox state of mantle play an important role in the formation of carbon species in the terrestrial basalts as well as in the composition of gases,evacuated by these liquidus to the upper layers of the Earth. It is expected, that interaction between native carbon and production of partial melting of the upper mantle : $C(graphite,diamond) + O^{2-}(melt) + O_2 = CO_3^{2-}(melt)$ (1) leads to the formation of CO_3^{2-}(carbonate ion) in melt [1,2]. Next mechanism, that may control the presence of free carbon and the formation of *C*-bearing components in magmas, is the carbon solubility in minerals under mantle conditions by participating in point defect equilibria.

CARBON AND CARBON-SATURARED FLUID IN UPPER MANTLE. Data on the oxygen fugacities (fO_2) recorded by mantle rocks show that the primitive and less modified spinel lherzolites may be in equilibrium with free carbon [3,4,5]. Electrochemical measurements of the intrinsic fO_2 of coexisting minerals (Ol,OPx,CPx,Spl,Gar) of spinel,garnet peridotite and diamond-bearing peridotite xenoliths indicate that the upper mantle beneath continent is characterized by a wide range of redox conditions, mainly in the range between the NNO and IW buffers [5]. Some primitive and less modified nodule suits brought to the surface in kimberlites and alkali basalts is estimated to be close to WM - IW buffers and correspond to the complete spectrum of *C-O-H* fluid saturated by carbon.This conclusion confirms by the presence of rare and extremely fine-graned crystals in minerals and carbon dissolved in olivines and pyroxenes (5-100 *ppm*)[5]. In this context,highly reduced peridotites may be interpreted as a relict from earlier lower fO_2 regime in the outer carbon-bearing layers of primitive Earth.

INTERACTION BETWEEN CARBON,CRYSTALS AND MELT. The experiments were made on C(graphite)-melt-crystals equilibria for *C + basaltic melt, C + basaltic melt + CPx* at 15-30 kbar and 1350-1400°C and on $C + Mg_2SiO_4$, $C + Mg_2SiO_4$ *+ melt,* $C + Mg_2SiO_4 + (CO-CO_2)$ *vapor+melt* for $CaMgSi_2O_6-Mg_2SiO_4$ composition at 25-40 kbar, 1400-1700°C.The solubility of carbon in crystals and silicate melts was determined by registration of the beta activity from ^{14}C) [2]. Experiments show, that carbon may be soluble in forsterite and pyroxene on concentration of 10-100 *ppm*. The coefficient of distribution *D* = (*C* in melt/*C* in crystal) equals about 10-100. Thus carbon is incompatible element in the melt + crystals equilibria and during the fluid-absent partial melting magma will be enriched in carbon in comparison with crystalline rest. The reaction between graphite and basaltic melt leads to the formation of 0.04-0.40 % *wt.* CO_2 in melt, observed generally in basaltic glasses.

It may be suggested, that the carbon-melt-crystal reactions during *1*) fluid - absent melting in presence some amount of free carbon (*carbon saturated equilibrium of melt+crystals+graphite*) and *2*) fluid- absent melting of carbon-bearing minerals (*carbon unsaturated equilibrium of melt+carbon-bearing minerals*) may be reason of the carbon-species formation in basaltic magmas.

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DYNAMICS OF VOLATILE DELIVERY FROM OUTER TO INNER SOLAR SYSTEM.
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Owen et al. [1] propose that the Ar excess of Venus compared to Earth was caused by impact of a large icy planetesimal from the outer solar system, where temperatures were low enough for Ar to adhere to ice, about 30 K. A body of solar Ar/Si and C/H similar to Pluto and Triton less than 100 km diameter would suffice.

However, direct delivery from the Uranus-Neptune zone to Venus would result in a very high approach velocity, causing erosion rather than accretion of volatiles. It would also be an extremely improbable event. Virtually all icy bodies scattered from the Uranus-Neptune zone to the terrestrial zone were strongly perturbed by Jupiter, but even then arrived at Venus (or Earth) at too-high velocities. What is needed is a "deboost" of bodies scattered inward from Jupiter by Earth and Venus perturbations, prior to impact into Venus. This has low probability, since the influence radii of Venus and Earth for the high velocities are small compared to that of Jupiter for the lower velocities further out.

It is desirable that this problem be examined by an integerator that allows for close approaches, such as developed by Levison and Duncan [2]. However, it would be a long and expensive computation compared to explaining short-period comets to accomplish the third "deboost" phase. But since close encounters dominate in such distant scattering, an Opik algorithm seems the appropriate reconnaissance tool.

Initial results from an Opik algorithm starting with bodies in the Uranus-Neptune zone, a = 18 to 40 AU, obtain about 0.2% scattered to the Jupiter-Saturn zone. Then, of this population, 1.5% get scattered so that their perihelia are less than 1.3 AU. However, 12 km/s was the lowest approach velocity of impacting Earth or Venus. The next phase was to retain only bodies whose aphelia were reduced inside Jupiter's orbit, 5.2 AU. These were 0.1% of those with perihelion below 1.3 AU. But still the minimum aphelion obtained was 2.6 AU, and the minimum approach velocities were, respectively, 8.6 km/s to Earth and 10.3 km/s to Venus.

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Phase E in a Water-Saturated Peridotite System at 9.3 GPa

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The stability of hydrous phases in a natural upper mantle system has been investigated at 9.3 GPa using a gel of KLB-1 peridotite composition (Takahashi, 1986, J. Geophys. Res.) with brucite which contains 14 wt. % (30 atom. %) water. No hydrous mineral was found at 950 (+150 -50) degree C. At 800 degree C, an assemblage of phase A, phase E, enstatite, clinohumite, and garnet is obtained. Although there is a significant thermal gradient over the sample, phase E is found to be surrounded by phase A in the lower temperature part. Electron probe analyses show that phase E has 35.5 SiO_2, 4.4 Al_2O_3, 41.1 MgO and 8.5 wt. % FeO* (Mg value is 90) with an oxide sum of 89.7 wt. %, and possesses a stoichiometry similar to that proposed by Kanzaki (1991, Phys. Earth Planet. Inter). CaO and TiO_2 are both less than 0.1 wt. %. Coexisting phase A has 0.5 wt. % CaO but only 0.4 wt. % Al_2O_3 concentration. Phase A coexists with only enstatite in the water-saturated MgO-FeO-SiO_2 system at 800 degree C and 9.3 GPa as well as the results in the water-saturated MgO-SiO_2 system (Yamamoto and Akimoto, 1977, Am. J. Sci). Therefore it is suggested that the addition of Al_2O_3 expands the stability field of phase E to lower than 13 -17 GPa in the water-saturated MgO-SiO_2 system (Kanzaki, 1991).

Phase A, phase E, and clinohumite can be formed in the Earth's upper mantle if the temperature, pressure, and water fugacity conditions allow them in the nature. There are no hydrous minerals at 9.3 GPa and 950 degree C in the water-saturated peridotite system. Therefore it is unlikely that phase A, phase E and clinohumite crystallized during the cooling of the Earth's magma ocean. In the subducting peridotite and the overlying wedge mantle, pargasite and phlogopite can be stable at levels shallower than 3 and 6 GPa, respectively (Tatsumi, 1989, J. Geophys. Res.). Previously proposed candidates for water-carrier to deeper mantle are K-richterite (Tatsumi, 1989) and phase A (Yamamoto and Akimoto, 1977). The appearance of phase E stabilized by Al_2O_3 at unexpectedly low pressure warrants further study, in order to determine whether phase E could act as an important water carrier to the deeper mantle.

NITROGEN ISOTOPIC COMPONENTS IN THE EARLY SOLAR SYSTEM

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It is quite common to take the terrestrial atmospheric value of $^{15}N/^{14}N$ (0.00366) as typical of nitrogen in the early solar system, but in fact there is little reason to suppose that this value had a nebula-wide significance. Indeed, it is not clear that there was a unique solar-system-wide $^{15}N/^{14}N$ ratio, of whatever value. Here we review what is known about the distribution of the nitrogen isotopes among those solar-system objects that have been sampled so far and conclude that those isotopes reveal widespread inhomogeneity in the early solar system. Whether the isotopically distinct primordial components implied by this analysis were solid or gaseous or a mixture of both is not known.

The isotopic composition of N in the Earth's mantle is controversial: estimates range from a 1.1% depletion in ^{15}N to a 1.4% enrichment [1,2]. (Isotopic compositions will be expressed throughout as percent deviations from the terrestrial atmospheric value.)

The present-day Martian atmosphere is characterised by a value of +62% [3] but this enrichment in ^{15}N is attributed to selective loss of ^{14}N from the Martian exosphere [4]. Modelling of this fractionation leads to an estimated primordial composition similar to the terrestrial atmospheric value [4], though the precision of this model-dependent result is unclear.

Indigenous lunar N is believed to have a $^{15}N/^{14}N$ ratio between 0 and +1.3% [5,6]. However, the lunar regolith, which contains several orders of magnitude more N than a typical lunar rock, exhibits a very wide range in $^{15}N/^{14}N$ ratios, ranging from -28% to >+15% [7]. The abundance of this regolith N correlates strongly with measures of surface exposure, including abundances of elements known to be implanted in the lunar surface by the solar radiation (solar wind and higher-energy particles). Consequently, much if not all of the regolith N is believed to consist of implanted solar radiation, though a non-solar source is also sometimes invoked [e.g.,8]. Stepwise analysis of an individual regolith sample reveals substantial variability in $^{15}N/^{14}N$, indicating presence of isotopically distinct components spanning a range of at least 20% [7]. Even more striking, bulk regolith values vary systematically with surface-exposure epoch, a trend revealed also by at least one of the major constituent components [7]. Bulk values start close to the terrestrial atmospheric value about 3.4Gyr ago, reach a minimum of about -20% at 1.8Gyr BP, then increase to about +10% at about 800Myr BP, possibly declining thereafter to about +4% at present. The cause of these changes is unknown. Possible explanations include: (a) long-term changes in the solar photospheric value, (b) mixing of isotopically distinct reservoirs in the sun, (c) long-term changes in fractionation of the solar radiation, and (d) mixing of solar N with a hypothetical non-solar component on the lunar surface. All of these explanations conflict with either observational data or established models of solar structure, evolution or radiation [7]. Pending resolution of this issue, generalisations about the isotopic composition of "solar-system N" are frought with uncertainty.

Analyses of meteorites reveal an even wider spread in $^{15}N/^{14}N$ values than observed in the lunar regolith, from -15% to +160%, Fig. 1. No systematic pattern is apparent in the data, except that most meteorite groups, defined by chemical/petrographic criteria, exhibit fairly similar $^{15}N/^{14}N$ ratios. Note that several meteorite groups contain quite high concentrations of N. In most cases, its chemical form is ill-defined, though in carbonaceous chondrites it is predominantly combined in organic matter such as amines, amides, and amino acids. The mechanism(s) by which meteorites, and for that matter the terrestrial planets, acquired their N is/are poorly understood. Based on thermochemical considerations, condensation would have led to N concentrations no

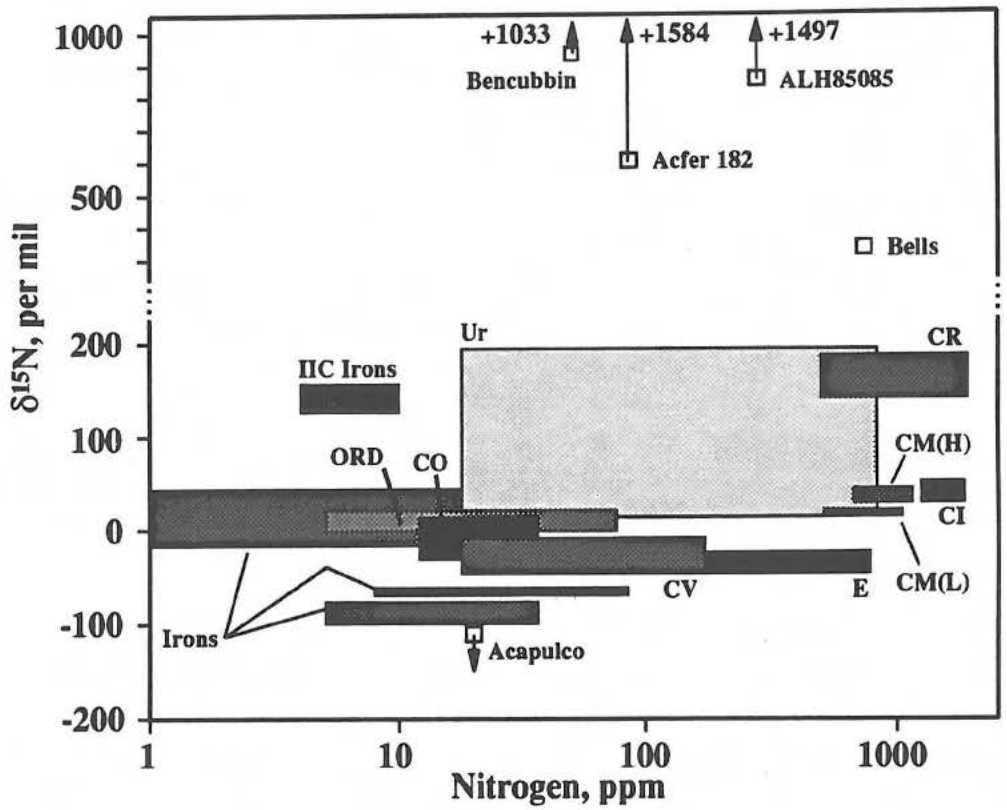

Figure 1. Nitrogen abundances and isotopic compositions for different meteorite classes and some anomalous meteorites identified by name. Isotopic compositions expressed in delta notation, i.e., as deviations in parts per thousand from the terrestrial air standard.

higher than a few ppm [9], suggesting that ices and/or organic matter, possibly of cometary or interstellar (if those terms are not synonymous) origin, were involved. Clearly, the meteorite data fail to provide support for a solar-system-wide $^{15}N/^{14}N$ ratio, and in fact point strongly towards a dramatic level of inhomogeneity among N isotopes in the solar nebula. (Note that this inhomogeneity is probably unrelated to the enormous range of $^{15}N/^{14}N$ ratios observed in individual interstellar carbonaceous grains isolated in trace quantities from primitive meteorites [10].)

Attempts have been made to measure $^{15}N/^{14}N$ in comets [11] and in the Jovian atmosphere [12], but in both cases observational uncertainties encompass most of the values discussed above. However, that situation should improve markedly in the next few years.

We conclude that several quantitatively major, isotopically distinct components of N were present in the early solar system. Their origin and distribution, their chemical and isotopic compositions, and even whether they were solid or gaseous, are very poorly defined at this time, precluding immediate application of the N isotopes to the distribution of volatile-rich material in the solar nebula. However, the other side of the coin is that, if we become successful at identifying those components, they may well serve as powerful tracers of such preplanetary volatiles.

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VOLATILES, RHEOLOGY, AND MANTLE CONVECTION: COMPARING EARTH, VENUS, AND MARS

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Silicate rheology is controlled in part by volatile content. The variation of viscosity with position in the mantle will influence the nature of mantle convection; hence, modeling mantle convection and its effect on surface observables such as the geoid places constraints on the viscosity structure of a planet's mantle and may indirectly constrain the volatile distribution. Models of viscous mantle flow and the Earth's geoid indicate that there is roughly a two order of magnitude variation in viscosity between the upper and lower mantles [e.g., 1,2], although there is some disagreement over the depth of the viscosity minimum in the upper mantle. Some studies of post-glacial rebound also support such a viscosity contrast between the upper and lower mantles. On Venus, several highland regions appear to be supported by mantle plumes. Modeling of the geoid and topography of these regions indicates that if these features are plume-related, then the mantle of Venus can not have an Earth-like low viscosity zone in its upper mantle [3]. On Mars, the Tharsis volcanic province has alternatively been explained as supported either by mantle convection or by flexure of a thick lithosphere. If the convective model is correct, then the large geoid anomaly requires that Mars can not have a low viscosity zone in its upper mantle [4].

One plausible explanation for these differences in the viscosity structures of the three planets involves differences in the mantle water content. On Earth, water is outgassed from the mantle by volcanism and may return to the mantle by subduction of hydrous minerals. On Venus, the high surface temperature prevents the formation of hydrous minerals. Outgassed water should therefore enter the atmosphere and be permanently lost from the interior. On Mars, there is strong geomorphic evidence for abundant water in the crust. However, there is no evidence that near-surface crustal material has been subducted on Mars in the last several billion years, so outgassed water may have been effectively lost from the interior there. The rheology of olivine is a strong function of the presence or absence of water [5], so the differences in the ability of the three planets to return outgassed water to the interior provides one explanation for the differences in viscosity structure inferred by geoid modeling. This model does require some method of confining the effect of water on rheology to the Earth's upper mantle. One possibility is that water does not partition as efficiently into high pressure phases as it does into low pressure phases, so that the deep mantles of all three planets are dry. Alternatively, water could have less effect on the rheology of high pressure phases than it has on the rheology of low pressure phases, in which case the geoid would be insensitive to the deep mantle volatile content.

Geoid modeling can constrain only the relative variation of viscosity with depth in a planet. Constraining the absolute viscosity requires other considerations, such as heat flux. Because of their similar size, Venus and Earth are commonly assumed to have similar overall heat flows. Because this heat is transported convectively within the mantle, this requires that the two planets have similar volume-averaged mantle viscosities. With a weaker increase of viscosity with depth on Venus than on Earth and the same depth-averaged viscosity, this requires that the upper mantle of Venus is more viscous than Earth's upper mantle in an absolute sense. Olivine rheology is well represented by a homologous temperature relationship [6], so the higher viscosity in the upper mantle of Venus implies that it is further from its melting point than Earth's upper mantle, despite the considerably higher surface temperature on Venus. This suggests that magmatic activity may occur at a lower rate on Venus than on Earth, consistent with Magellan observations [7].

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SUBDUCTION AND VOLATILE RECYCLING IN EARTH'S MANTLE. S. D. King[1], J. J. Ita[2], and H. Staudigel[3], [1]Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907, USA, [2]252-21 Seismological Laboratory, Caltech, Pasadena, CA, 91125, USA, [3]Vrije Universiteit, Laboratory for Isotope Geology, Faculty for Earth Sciences, 1081 HV Amsterdam, The Netherlands.

The subduction of water and other volatiles into the mantle from oceanic sediments and altered oceanic crust is the major source of volatile recycling in the mantle. Until now, the geotherms that have been used to estimate the amount of volatiles that are recycled at subduction zones have been produced using the hypothesis that the slab is rigid and undergoes no internal deformation [1]. On the other hand, most fluid dynamical mantle flow calculations assume that the slab has no greater strength than the surrounding mantle [2; 3]. Both of these views are inconsistent with laboratory work on the deformation of mantle minerals at high pressures [4].

We consider the effects of the strength of the slab using two-dimensional calculations of a slab-like thermal downwelling with an endothermic phase change. Because the rheology and composition of subducting slabs are uncertain, we consider a range of Clapeyron slopes which bound current laboratory estimates of the spinel to perovskite plus magnesiowüstite phase transition and simple temperature-dependent rheologies based on an Arrhenius law diffusion mechanism. In uniform viscosity convection models, subducted material piles up above the phase change until the pile becomes gravitationally unstable and sinks into the lower mantle (the avalanche). Strong slabs moderate the "catastrophic" effects of the instabilities seen in many constant-viscosity convection calculations; however, even in the strongest slabs we consider, there is some retardation of the slab descent due to the presence of the phase change.

There are two pronounced effects that phase changes have on subducting slab geotherms. First, phase changes cause the vertical velocity of slabs to decrease during the period when material is piling up above the phase change, compared to simple models with no phase changes. If the slab is weak, this can lead to large deformation, even in the upper 200 km of the slab. Second, the phase change effects the subduction velocity; a more pronounced effect than that of slab deformation. During the pile-up period, the slab geotherm is characteristic of geotherms produced by steady-state slab models with slow plate velocities. However, during the avalanche period when the material that has been stored above the phase change begins to flush into the lower mantle, the subducting slab geotherm approaches the geotherms from steady-state models with fast or ultrafast velocities [5]. The difference between the subducting slab velocities of the two periods (the pile-up period and the avalanche period) decreases with increasing viscosity of the slab. Because the initial thermal structure of descending lithosphere, the volatile content, and subduction velocity all effect the viscosity of the slab, it is quite likely that certain subduction zones may behave quite differently than others, some with more pronounced pile-up and avalanche periods and some where the subduction velocity is much more uniform with time.

These mechanisms create a highly uneven distribution of recycled components in the mantle within relatively short periods of time in earth's history. We speculate that the resulting uneven distribution of volatiles in the mantle may cause localized viscosity reduction, which may provide a critical boundary condition for the initial rise of mantle plumes. Furthermore, these results also explain the uneven distribution of recycled components in the mantle as it is demonstrated on the basis of Sr, Nd and Pb isotopic data from ocean intraplate basalts. The consistent explanations of geochemical and geophysical data support our model and they testify to the non-steady state character of mantle circulation.

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VOLATILES IN THE DEEP EARTH: AN EXPERIMENTAL STUDY USING THE LASER-HEATED DIAMOND CELL. Xiaoyuan Li[1], Raymond Jeanloz[1] and Jeffrey H. Nguyen[2] [1]Department of Geology and Geophysics, University of California, Berkeley, CA 94720, USA, [2]Department of Physics, University of California, Berkeley, CA 94720, USA.

Experiments with the laser-heated diamond cell show that H_2O and CO_2 can be stabilized within crystalline mineral structures of the lower-mantle, and hence can be present as relatively non-volatile components of the Earth's deep interior. Samples quenched from high pressures and temperatures document that the $MgCO_3$-$FeCO_3$ magnesite-siderite solid-solution is stable and coexists with $(Mg,Fe)SiO_3$ perovskite at 30-40 GPa and ~1500-2000 K. In contrast, H_2O combines with the silicate to form $(Mg,Fe)SiH_2O_4$ phase D [1], coexisting with $(Mg,Fe)SiO_3$ perovskite at these conditions [2]. If enough water is present, phase D can become the predominant phase in the $MgSiO_3$-H_2O system at lower-mantle conditions. Our work extends previous studies to Fe-bearing compositions and to the pressures of the mid-lower mantle [3, 4]. Thus, the results of high-pressure experiments suggest that both H_2O and CO_2 can be abundant in the Earth's lower mantle, being present in stable hydroxisilicate and carbonate phases.

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ALKALI ELEMENT DEPLETION BY CORE FORMATION AND VAPORIZATION ON THE EARLY EARTH.
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Synopsis. The depletion of Na, K, Rb, and Cs in the Earth's upper mantle and crust relative to their abundances in chondrites is a long standing problem in geochemistry [1,2]. Here we consider two commonly invoked mechanisms, namely core formation, and vaporization, for producing the observed depletions. Our models predict that a significant percentage of the Earth's bulk alkali element inventory is in the core (30% for Na, 52% for K, 74% for Rb, and 92% for Cs). These predictions agree with independent estimates from nebular volatility trends [3] and (for K) from terrestrial heat flow data [4]. Our models also predict that vaporization and thermal escape during planetary accretion are unlikely to produce the observed alkali element depletion pattern. However, loss during the putative giant impact which formed the Moon cannot be ruled out. Experimental, observational, and theoretical tests of our predictions are also described.

Core Formation. Alkali element partitioning into the Earth's core was modeled by assuming that alkali element partitioning during core formation on the aubrite parent body (APB) is analogous to that on the early Earth [5]. The analogy is reasonable for three reasons. First, the enstatite meteorites are the only known meteorites with the same oxygen isotope systematics as the Earth-Moon system. Second, the large core size of the Earth and the V depletion in the mantle requires accretion from planetesimals as reduced as the enstatite chondrites [5-7]. Third, experimental studies of K partitioning between silicate and metal + sulfide show that more K goes into the metal + sulfide at higher pressures than at one atmosphere pressure [8]. Thus partitioning in the relatively low pressure natural laboratory of the APB is a good guide to alkali elemental partitioning during the growth of the Earth.

The aubrites represent the silicate portion of the aubrite parent body and contain minor amounts of metal and alkali rich sulfides such as djerfisherite (10 wt.% K) and caswellsilverite (16 wt.% Na) which apparently failed to migrate into the core. Mass balance calculations [5] using the bulk (EH-chondrite) composition of the APB and the composition of the APB mantle (aubrites) show that the core of the aubrite parent body contains 2590 ppm Na, 550 ppm K, 3.4 ppm Rb, and 0.31 ppm Cs. The same alkali element abundances were taken for the Earth's core. Published estimates of alkali element abundances in the bulk silicate Earth [3,6] were combined with the estimated abundances in the Earth's core to predict bulk Earth (core + mantle + crust) alkali element abundances of 2800 ppm Na, 340 ppm K, 1.5 ppm Rb, and 110 ppb Cs. The fractions of each alkali in the core are given above, and agree with independent published estimates [3-4]. We note that prior partitioning experiments do not provide good constraints on alkali element partitioning into either the core of the APB or the Earth's core because inappropriate compositions and oxygen fugacities were used. However, the calculated bulk Earth abundances of the alkalis are only 40% (Na), 43% (K), 50% (Rb) and 80% (Cs) of those found in ordinary chondrites suggesting either an additional loss process or another unidentified host phase (e.g., in the lower mantle).

Vaporization. Two important factors control alkali loss by vaporization during planetary accretion and differentiation. First, temperatures must rise high enough to evaporate alkali elements and their compounds. Second, the gaseous vapors must leave the gravitational field of the (growing) planetary body. Vaporization of the alkalis can be calculated using the MAGMA code [9], while thermal (Jeans) escape is governed by the ratio of the thermal velocity (v_{th}) of the gaseous species to the planetary escape velocity (v_{esc}). Two cases (v_{esc}/v_{th} = 1; 5) were considered at the Fe-FeS eutectic temperature of 1270 K where planetary differentiation begins [10]. The results show that alkali loss is negligible from Mars sized and larger bodies under these conditions. However, alkali loss during the putative Moon-forming impact has not yet been modeled and cannot be ruled out. If alkali elements were completely vaporized from the mantle by the impact, the lighter alkali elements are more likely to move out of the gravitational field of the Earth-Moon system. This could explain the relative increasing abundances from light to heavy alkali elements calculated for the bulk Earth above.

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THE RATIOS OF CARBON AND NON-RADIOGENIC HELIUM AND ARGON ISOTOPES IN THE MANTLE AND CRUSTAL ROCKS. K. Lokhov and L. Levsky, Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, Makarova emb., 2, St. Petersburg, 199034, RUSSIA.

The studies of the relations of carbon and primary isotopes of noble gases were carried out on the natural gases (1) and on the mantle rocks from the mantle M-type sources, which represent the degassed mantle reservoir (MORBs) (2). These works had the aim of estimation of the values of the C/3He ratios in the deep mantle fluids to determine the flux of the mantle CO2 on the basis of known flux of primary mantle 3He.

It was found, that in the natural gases the values of the C/3He ratios fall into the range from 1*E+6 to 1*E+15, and in the fluids of MORB's are constant near 2*E+9.

We have studied the mantle rocks from the relatively undegassed mantle P- type sources: continental; Baikal Rift (Siberia), Mongolia, Catalonia (Spain), Pannonia Depression (central Europe) and ocean; Spietzbergen isl., Hawaii isl., Canarian isl.

It was found, that in mantle xenolites and the host alkaline basalts from the continental rifts and ocean islands, the the values of the C/3He ratios fall into the range from E+11 to E+15 (and this result needed to be explained; the higher carbon to helium ratios in relatively undegassed mantle reservoir compared with the degassed one, requires whether hilly compatibility of helium compared with carbon !, whether additional flux of 3He to the degassed mantle reservoir). From the other hand it was found that in the mantle rocks from the sources of P- and M- types, continental carbonatites, the values of the C/36Ar ratios are constant in the range from E+9 to E+10, the close values have the MORB's also.

We suggest, that in the continental crust the values of the C/36 Ar ratios can be only lower, than in the mantle, because of the presence in the crust, as mantle originated rocks, so sedimentary, formed in the hydrosphere with low (down to E+6) C/36Ar ratios.

Our data upon the sedimentary phanerozoic rocks and metamorphic precambrian rocks do confirm this hypotesis.

The glaukonites from Cambrian-Devonian sandstones have the values of the C/36Ar ratios in the range n*E+7, metamorphic amphibolite and granulite facies precambrian rocks from Kola peninsula and Northern Karelia- in the range: n*E+7-E+9.

So, the criteria of presence of the mantle component in crustal fluids, based on the value of the C/36Ar ratio, could be developed. This criteria could be especially suitable for the studies of ancient rocks, where the isotopic compositions of primordial He are distorted due to accumulation of the radiogenic isotopes.

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SOLAR SYSTEM FORMATION AND THE DISTRIBUTION OF VOLATILE SPECIES

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To understand how the solar system formed we must understand the compositional distribution of the current system. Volatile species are particularly important in that their stability as condensed phases is limited in temperature-pressure space, and hence variations in their distribution at present potentially contain an imprint of processes by which temperature and pressure varied in the solar nebula. In this talk we restrict ourselves to species more volatile than water ice, and address issues related to processes in the outer solar system and the formation of bodies there; others in this conference will cover volatile species relevant to inner solar system processes. Study of the outer solar system is relevant both to understanding the interface between the solar nebula and the progenitor giant molecular cloud (since the chemical links to present-day observables in molecular clouds are species like methane, carbon monoxide, etc.), as well as the origin of terrestrial planet atmospheres and oceans (the latter to be covered by Owen). The wealth of compositional information on outer solar system bodies which has become available from spacecraft and ground-based observations challenges traditional simplistic views of the composition and hence dynamics of the solar nebula. The basic assumption of thermochemical equilibrium, promulgated in the 1950's, in which methane and ammonia dominate nitrogen-and carbon-bearing species, is demonstrably incorrect on both observational and theoretical grounds. However, the kinetic inhibition model which replaced it, in which carbon monoxide and molecular nitrogen dominate a nebula which is fully mixed and hence cycles outer solar system gases through a hot, chemically active zone near the disk center, is not supported either by observations. Instead, a picture of the outer solar system emerges in which the gas and grains are a mixture of relatively unaltered, or modestly altered, molecular cloud material, along with a fraction which has been chemically altered in the solar nebula itself (and perhaps giant planet nebulae). Processing of volatiles has occurred to the present-day on all but the smallest of outer solar system bodies. Theoretical models raise a number of issues regarding the history of volatile species in the solar nebula. A partial list includes: 1. Dynamical and chemical processes acting on water vapor and other condensables within the nebula can lead to temporal and spatial dependences which are complex, and depend on transport both in the gaseous and solid phases; 2. Infall of grains from the molecular cloud leads to heating, sublimation, and a limited amount of chemical reactions within the grain. The amount of heating depends both on the radial distance at which the grain intersects the surface of the disk, as well as the physics of the interface between the disk and molecular cloud. 3. Volatiles in the gas phase in the nebula can be trapped by water ice, but the trapping process is sensitively dependent on the conditions in the nebula, as well as grain size, frequency of grain-grain collisions, and other factors. While laboratory experiments provide critical constraints on the trapping process, they cannot hope to cover enough of the range of conditions to serve as predictive guides by themselves. Sound theoretical models of grain trapping, underpinned by the lab data, are essential. Observations support the complex view of a dynamic solar nebula and early solar system: 1. The volatile budgets of Titan, Triton and Pluto are not readily explainable as unaltered remnants of volatile budgets in their respective regions of formation. Titan's density and abundance of methane are suggestive of formation in a high pressure, reducing nebula around Saturn, but the predominance of molecular nitrogen in the atmosphere is not. Photochemical or thermochemical conversion of ammonia to nitrogen is plausible, but detection of crustal ammonia by Cassini would be helpful in buttressing this view.

Because Titan is protected by a thick atmosphere ammonia flows might survive on its surface in contrast to that of smaller satellites where solar UV has photolytically destroyed the ammonia in the optical surface layers. An alternative model for the formation of Titan's atmosphere by cometary impact requires a mechanism for loss of large amounts of carbon monoxide while retaining methane. Triton and Pluto both have nitrogen-dominated surface volatile budgets. Carbon monoxide is expected to dominate over nitrogen, based on elemental abundance, plausible molecular compositions for outer solar nebula gas and trapping propensities in primordial grains, but turns out to be of minor abundance on these surfaces. Aqueous alteration of carbon monoxide in the interiors of these bodies is possible if heating is sufficient to melt water ice; tidal heating does this on Triton but the mechanism for Pluto is unclear. Alternatively, formation of a massive early atmosphere, and loss to space of the early volatile budget, could lead to the present distribution provided that ammonia is again the source of the molecular nitrogen; such a model remains to be quantified. 2. Comets have a volatile budget which is consistent with what is known about grains and gas in molecular clouds, and hence could set constraints on the degree of alterations of grains falling into the solar nebula. However, the location within the nebula at which comets formed is uncertain, so their utility in setting constraints on solar nebula conditions is extremely limited. Future missions in which the structure of the water ice and mechanisms for trapping of volatiles in the cometary grains represent important prospects for further constraining outer solar nebula conditions.

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SOLUBILITIES OF NITROGEN AND NOBLE GASES IN BASALT MELT.

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Nitrogen and noble gases are important tracers in geochemistry and chosmochemistry. Compared to noble gases, however, physicochemical properties of nitrogen, such as solubility in melt or melt/silicate partition, are not well known.

Solubility of nitrogen in basalt melt depends on redox condition of the atmosphere [1]. For example, solubility of nitrogen in E chondrite melt under reducing conditions is as high as 2 mol% at 1500°C [2], suggesting that nitrogen is chemically dissolved in silicate melts, i.e., being dissolved as free anions or replacing oxygen sites in silicate network (e.g. [3],[4]). However, the solubility and the dissolution mechanism of nitrogen under oxidizing conditions are not well investigated.

To obtain nitrogen solubility in silicate melts under various redox conditions and to understand its mechanism, we are conducting experiments by using $^{15}N^{15}N$-labeled nitrogen gas. This makes it easy to distinguish dissolved nitrogen from later contamination of atmospheric nitrogen, and hence enables us to measure the nitrogen solubility accurately. As a preliminary experiment, we have measured solubility of nitrogen in basalt melt under the atmospheric oxygen pressure.

(1) Experimental

First, basalt powder was perfectly melted and degassed under vacuum and quenched to make starting material. The basalt glass was cut into thin plates (about 0.5 mm thick) and remelted on a piece of platinum mesh at 1300°C under atmosphere of $^{15}N^{15}N$-labeled air (P[total] = 1 atm and P[oxygen] = 0.21 atm). The "$^{15}N^{15}N$-labeled air" is a mixture of normal air and $^{15}N^{15}N$ gas, and has about 550 times higher $^{15}N^{15}N$ concentration than that of normal air. The basalt melt was quenched after 6 hours heating. The quenched glass samples were analyzed with quadrupole-type mass spectrometers.

(2) Results

Solubility (Henry's constant) of nitrogen in basalt melt is calculated to be 4.4×10^{-5} ccSTP/g/atm (2.9×10^{-9} mol/g/atm) from the recovered non-atmospheric ^{15}N and its partial pressure of $^{15}N^{15}N$ in the gas phase once equilibrated with the basaltic melt. This is comparable to that of argon obtained in our previous study (2.1×10^{-5} ccSTP/g/atm, [5]). The present result shows that solubility of nitrogen seems to be almost equal to that of argon under oxidizing condition.

The recovered nitrogen gas was highly enriched in $^{15}N^{15}N$, like the $^{15}N^{15}N$-labeled gas used in this experiment. Nitrogen in both of the gases were isotopically not in equilibrium, that is, ratios of mass 28:29:30 in the gas are not $1:2r:r^2$, where $r = {}^{15}N/{}^{14}N$. If nitrogen dissolves in the melt as anions or atoms, such disequilibrium in the original gas would easily disappear and not been taken over by the recovered gas. Hence, the highly enriched $^{15}N^{15}N$ observed in the recovered gas suggests that most of nitrogen was dissolved in basalt melt as molecules under highly oxidizing condition.

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SEISMIC EVIDENCE FOR VOLATILES AT LARGE DEPTH IN THE EARTH.
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High resolution tomographic images that have been obtained of the subduction zones in the west Pacific [1,2] do not only show very low P wave velocities above the leading edge of the slab at shallow depth, but also below 300 km. The two zones are generally - but not always - separated by a zone of normal shear velocity near 200 km depth. These findings confirm some earlier inferences from local seismic data in Japan [3], and similar findings of low Vp and low Q zones beneath South America.

Surprisingly, such deep seismic low velocity zones have recently also been discovered beneath the locations of ancient subduction zones. A study of upper mantle shear velocity in Central Europe [4] shows a similar distribution of low velocity zones beneath the Tornquist-Teisseyre line, the former west coast of the old continent of Baltica, and the site of the subducting Tornquist ocean in the early Paleozoic. Preliminary results from a Russian-French experiment shows low P velocities below 250 km under the Urals, while an older tomographic study shows such low P velocities beneath the northern Appalachians [5].

Whereas the low velocity zones near 100 km depth are easily explained in terms of dehydration of common hydrous phases and subsequent melting of a small part of the rock, the deeper low velocities require a more complicated mechanism. The amplitude of the S velocity anomalies is too large to be caused by compositional differences or by direct effects of temperature, but either partial melting or the velocity dispersion that must accompany high attenuation of seismic waves can be responsible. Either mechanism would require that the solidus of the rock is appreciably lowered below that for dry peridotite.

A possible mechanism to bring volatiles to large depth is offered by the 'alphabet' phases, a series of dense hydrous magnesium silicates (DHMS) with a stability field extending to high pressure in the cold regime of a subduction zone. A comparison of the low velocity profile near active subduction zones correlates well with laboratory determinations of the stability fields for the DHMS. Rough estimates of the amount of water transported down a subduction zone show that a sufficient concentration of volatiles may easily accumulate in large pockets in the ambient mantle to produce free water or partial melt when the rock warms up, e.g. by the passage of a hotspot.

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RATES OF EARTH DEGASSING

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The degassing of the Earth during accretion is constrained by Pu-U-I-Xe systematics. Degassing was much more efficient during the first 100-200 Ma than subsequently, and it was more complete for Xe than for the lighter gases [3]. More than 90% of the degassed Xe escaped from the atmosphere during this period. The combination of fractional degassing of melts [1] and rare gas escape from the atmosphere [2] is able to explain the deficit of terrestrial Xe as a simple consequence of this early degassing history.

By the time Xe was quantitatively retained in the atmosphere, the abundances of Kr and the lighter gases in the Earth's interior were similar to or higher than the present-day atmospheric abundances. Subsequent transfer of these lighter rare gases into the atmosphere requires a high rate of post-accretion degassing and melt production. Considerations of Pu-U-Xe systematics suggest that relatively rapid post-accretion degassing was continued to ca. 4.1-4.2 Ga.

The present-day degassing history of the Earth is investigated through consideration of rare gas isotope abundances. Although the Earth is a highly degassed body, depleted in rare gases by many orders of magnitude relative to their solar abundances, it is at the present-day losing primordial rare gases which were trapped at the time of accretion.

The loss of rare gases from the Earth's mantle is directly related to mantle melting and the degassing of these melts at the surface. The present-day relationship between melting and degassing may be assessed given that the rare gases appear to behave as incompatible elements upon melting. It may eventually prove possible to relate evidence for higher loss rates of rare gases earlier in Earth history to amounts of mantle melting. It is difficult to reconcile the differences in the Ne and Ar isotope composition between basalts erupted at ridges and at plume sites with anything but a convectively layered mantle structure, and one that has been so for most of Earth history. The small amount of ^{3}He and other primordial isotopes of Ne and Ar in the present-day upper mantle are accounted for by entrainment from the lower mantle. In the latter case entrainment of only ~1% of the lower mantle mass per Ga is able to provide the ^{3}He inventory in the upper mantle. The residence time of He in this reservoir is estimated at ~1 Ga [3] which is very similar to earlier estimates for the highly incompatible lithophile elements, U, Th, Pb. However, the amount of these lithophile elements that accompany the introduction of ^{3}He into the upper mantle is too small to sustain their steady-state abundances. The continental lithosphere appears to be the major source of these lithophile elements.

These conclusions have implications for the behaviour of major volatiles such as C. These should also be influenced by recycling and C/^{3}He ratios in plume and ridge basalts may reflect this.

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COMETS, IMPACTS, AND ATMOSPHERES. Tobias Owen[1], and Akiva Bar-Nun[2], [1]Institute for Astronomy, University of Hawaii, 2680 Woodlawn Drive Honolulu HI 96822, USA, [2]Department of Geophysics & Planetary Sciences, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, ISRAEL.

Studies of element abundances and values of D/H in the atmospheres of the giant planets and Titan have emphasized the important role of icy planetesimals in the formation of these bodies [1]. In these atmospheres, C/H and D/H increase as the relative masses of the "cores" of the planets increase. N/H appears to deviate from this trend in an interesting way. In the inner solar system, the traditional approach of using carbonaceous chondrites as the source of planetary volatiles is in serious trouble because of the depletion of xenon and the unusual pattern of xenon isotopes found in the atmospheres of Earth and Mars, and because of the solar-type abundance ratios of argon, krypton and xenon and the large amounts of neon and argon on Venus [2]. Recent studies of elemental abundances in comets, especially P/Halley [3], coupled with laboratory studies of the trapping of gas in ice formed at low temperatures by A. Bar-Nun *et al.* [4] provide a consistent interpretation of all of these results [5]. This interpretation emphasizes the fundamental importance of icy planetesimals (comets) and the randomness of early impacts in the formation of planetary systems. Cometary delivery by itself will not explain the noble gas abundances on the inner planets. There is good evidence for at least one additional source, which presumably consists of the rocky material making up the bulk of the planets. The existence of this rocky reservoir is manifested in the nucleogenic isotopes and in the neon which is found in all these atmospheres and is also present in the Earth's mantle. This neon may well be a relic of the planets' earliest, accretional atmospheres.

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POLAR VOLATILES ON MERCURY AND THE MOON. D. A. Paige[1], S. E. Wood[1] and A. R. Vasavada[2], [1]Department of Earth and Space Sciences, UCLA, Los Angeles CA, 90024, USA, [2]Division of Geological and Planetary Sciences, Caltech, Pasadena CA 91125, USA.

The possibility that condensed volatiles might be stable in the permanently shadowed polar regions of the Moon and Mercury has been anticipated in a number of theoretical studies [1–4]. In 1992, VLA-Goldstone [5] and Arecibo [6] observations revealed the presence of bright, depolarized radar features near the poles of Mercury that have been widely interpreted as evidence for the presence of polar ice deposits [7,8]. Recently acquired high-resolution Arecibo radar images show that the anomalous radar features are concentrated in crater-sized regions whose locations can be made to coincide exactly with the locations of known impact craters in the Mariner-10 images [9]. These new Arecibo images provide an unusual opportunity to learn more about the distribution and history of Mercury's polar ice deposits.

We have constructed a thermal model that can predict surface and subsurface temperatures within impact craters on Mercury and the Moon. Included in the calculations are the effects of 1-dimensional subsurface heat conduction, direct sunlight, multiply reflected sunlight within the crater, and re-radiated infrared radiation within the crater. We also use realistic crater topographic profiles for larger flat-floored craters as well as smaller spherical bowl-shaped craters.

On Mercury, the results show that within the impact craters where anomalous radar features have been observed, bi-annual maximum surface temperatures can be as low as 56K, and as high as 150K. Within these same craters, there are regions below the surface where bi-annual maximum temperatures can be as low as 42K, and as high as 92K. Furthermore, the model results show that these low-temperature regions within the craters were clearly visible from Earth on the dates when the Arecibo radar maps were obtained. By comparing the model-predicted geographic distribution of these low-temperature regions with that observed by Aricebo, approximate maximum temperatures for the volatile materials responsible for the radar features can be estimated. If the volatile materials extend to the surface, then their maximum bi-annual temperatures must be approximately 150 K. If the volatile materials lie below the surface, covered by fine-grained soil that is characteristic of other regions on Mercury, then their maximum bi-annual temperatures must be approximately 90 K.

Analysis of our thermal model results has led us to the conclusion that water ice is the major volatile component of the polar deposits on Mercury. However, less volatile, cosmically abundant species such as NH3, CO2, H2S and their hydrates may also be present. The results also suggest that the deposits are protected by a relatively thin layer of soil, and have existed in their present states for billions of years, with little need for resupply due to evaporative loss.

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MANTLE RARE GAS RELATIVE ABUNDANCES IN A STEADY-STATE MASS TRANSPORT MODEL

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A model for He (Kellogg and Wasserburg, 1990) and Xe (Porcelli and Wasserburg, 1994) was presented previously which incorporates mass transfer of rare gases from an undegassed lower mantle (P) and the atmosphere into a degassed upper mantle (D). We extend the model to include Ne and Ar. Model constraints on rare gas relative abundances within P are derived. Discussions of terrestrial volatile acquisition have focused on the rare gas abundance pattern of the atmosphere relative to meteoritic components, and the pattern of rare gases still trapped in the Earth is important in identifying volatile capture and loss processes operating during Earth formation.

The assumptions and principles of the model are discussed in Wasserburg and Porcelli (this volume). For P, the concentrations in P of the decay/nuclear products ^{4*}He, ^{21*}Ne, ^{40*}Ar, and ^{136*}Xe can be calculated from the concentrations of the parent elements U, Th, K, and Pu. The total concentration of the daughter element in P is proportional to the isotopic shifts in P. For Ar, $(^{40}Ar/^{36}Ar)_P - (^{40}Ar/^{36}Ar)_O = \Delta^{40}_P = {}^{40*}C_P/{}^{36}C_P$, where ${}^iC_j$ is the concentration of isotope i in j. In D, isotope compositions are the result of mixing rare gases from P, decay/nuclear products generated in the upper mantle, and subducted rare gases (for Ar and Xe). For Ar, $(^{40}Ar/^{36}Ar)_D(1+\delta^{36}_{SUB})=(^{40}Ar/^{36}Ar)_P(1+\delta^{40}_{PR})+(^{40}Ar/^{36}Ar)_{ATM}(\delta^{36}_{SUB})$. The terms δ^i_{SUB} and δ^i_{PR} are the fractional increases of i in D due to subduction and production in D, respectively, where $\delta^{36}_{SUB} = \dot{M}_{SUB}\,{}^{36}C_{SUB}/[{}^{36}C_P(1-r)\dot{M}_{PD}]$ and $\delta^{40}_{PR}={}^{40}PM_D\,{}^{K40}C_D/[{}^{40}C_P(1-r)\dot{M}_{PD}]$. The term $(1-r)\dot{M}_{PD}$ is the rate at which P material not degassed at hotspots is mixed into D, and ${}^iP$ is the production rate of i per atom of parent nuclide in P. The isotopic shift in D relative to P is $\Delta^{40}_D=(^{40}Ar/^{36}Ar)_D - (^{40}Ar/^{36}Ar)_P$. Similar equations can be written for ^{4}He/^{3}He, ^{21}Ne/^{20}Ne, and ^{136}Xe/^{130}Xe (with $\delta^3_{SUB}=\delta^{20}_{SUB}=0$). From data of mantle-derived materials, He and Ne isotopic compositions can be assigned to D and P (see Kurz et al., 1983, Honda et al., 1991, Farley and Poreda, 1993) as well as Ar and Xe isotope compositions to D (see Sarda et al., 1985 and Staudacher and Allegre, 1989). The Ar and Xe isotope compositions in P and the concentrations of all the rare gases in P and D are not known.

From a consideration of the closed system equations for P and the mass transport equations for D, the following conclusions can be drawn: 1) The mantle isotope compositions of both He and Ne inferred from measured mantle isotope variations are compatible with the mass transport equations (see also Honda et al., 1991, Farley and Poreda, 1993, O'Nions and Tolstikhin, 1994) and are related by $\Delta^{21}_P/\Delta^{21}_D = \Delta^4_P/\Delta^4_D$. This is independent of the relative production rates of ^{4}He and ^{21}Ne as well as of the concentration of parent element abundances. Since $\Delta^4_P/\Delta^4_D \approx 0.3$, the fractional enrichment of ^{21}Ne in D relative to P is much greater than that of ^{21}Ne in P relative to initial Ne. 2) The ratio of ^{40}Ar in D derived from decay of K in D to the ^{40}Ar in D derived from P, is $\delta^{40}_{PR}=1.3$. The ^{36}Ar and ^{130}Xe in D may be accounted for by the subduction of atmospheric Ar and Xe. 3) From the equation for Ne in P, ${}^{20}C_P=\Delta^{21}_P/{}^{21*}C_P=1.6\times10^{11}$ atoms/g. From the equation for Ar in D (with $(^{40}Ar/^{36}Ar)_D >> (^{40}Ar/^{36}Ar)_{ATM}$), ${}^{36}C_P={}^{40*}C_P(1+\delta^{40}_{PR})/\ [(^{40}Ar/^{36}Ar)_D(1+\delta^{36}_{SUB})]$. For $(^{40}Ar/^{36}Ar)_D=28{,}000$ (Sarda et al., 1985) and ${}^{40*}C_P=5.7\times10^{14}$atoms/g, then $(^{20}Ne/^{36}Ar)_P = 3.4(1+\delta^{36}_{SUB})$, and $(^{20}Ne/^{36}Ar)_P$ is much greater than $(^{20}Ne/^{36}Ar)_{ATM}$ (=0.52), and is consistent with the trend in ^{20}Ne/^{36}Ar-^{20}Ne/^{22}Ne seen in meteorites (Mazor et al., 1970) as well as the assumption that 'solar' light rare gases are stored in the lower mantle (Honda et al., 1991). 4) From Porcelli and Wasserburg (1994), ${}^{130}C_P={}^{136*}C_P(1+\delta^{136*}_{PR})/\ [(^{136}Xe/^{130}Xe)_D(1+\delta^{36}_{SUB})-\delta^{130}_{SUB}(^{136}Xe/^{130}Xe)_{ATM}-(^{136}Xe/^{130}Xe)_O]$. Combining with the equation above for ${}^{36}C_P$ and substituting known values for isotopic compositions and production rates, $(^{36}C/^{130}C)_P = \delta^{130}_{SUB}(400-{}^{36}C_{SUB}/{}^{130}C_{SUB})+500$. For the case of no significant subduction of Ar and Xe into D ($\delta^{130}_{SUB}=0$), the ^{36}Ar/^{130}Xe ratio of the lower mantle is 20 times lower than $(^{36}Ne/^{130}Xe)_{ATM}$(=8640) and similar to the 'planetary' composition in meteorites (^{36}Ne/^{130}Xe=600). The calculated lower mantle ^{36}Ar/^{130}Xe ratio is greater if subducted atmospheric Xe is highly enriched (by 10^2 times) relative to Ar, and if a significant fraction of Xe in D is derived from subduction of atmospheric Xe. 5) If a large fraction of the total Ar in the upper mantle is subducted atmospheric Ar, then the ^{40}Ar/^{36}Ar of the lower mantle must be large. Similarly, if Xe in D is largely derived from subduction, then $(^{136}Xe/^{130}Xe)_P$ and $(^{129}Xe/^{130}Xe)_P$ must be large. Further observational constraints are required of rare gas subduction and lower mantle isotope compositions to determine whether the lower mantle exhibits the same depletion in Xe relative to Ar (and Kr) that is displayed by the terrestrial atmosphere relative to meteoritic compositions. Div. Contrib. 860.

HYDROGEN STORAGE IN EARTH'S MANTLE AND CORE. Charles T. Prewitt, Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA.

Two different approaches to explaining how hydrogen might be stored in the mantle are illustrated by a number of papers published over the past 25-30 years, but there has been little attempt to provide objective comparisons of the two. One approach invokes the presence in the mantle of dense hydrous magnesium silicates (DHMS) stable at elevated pressures and temperatures [1,2]. The other involves nominally anhydrous minerals (NAM) that contain hydrogen as a minor constituent on the ppm level [3,4]. Experimental studies on DHMS indicate these phases may be stable to pressures and temperatures as high as 16 GPa and 1200°C. This temperature is lower than that indicated by a mantle geotherm at 16 GPa, but may be reasonable for a subducting slab. It is possible that other DHMS could be stable to even higher pressures, but little is known about maximum temperature limits. For NAM, small amounts of hydrogen (up to several hundred ppm) have been detected in olivine, orthopyroxene, clinopyroxene, and garnet recovered from xenoliths in kimberlites, eclogites, and alkali basalts [4]; it has been demonstrated that synthetic wadsleyite and perovskite can accommodate significant amounts of hydrogen [5,6]. A number of problems are associated with each possibility. For NAM originating in the mantle, one would like to assume that the hydrogen measured in samples recovered on Earth's surface was incorporated when the phase crystallized at high temperatures and pressures, but it could have been introduced during transport to the surface. Major problems for the DHMS proponents are that none of these phases have been found as minerals and little is yet known about their stabilities in systems containing other cations such as Fe, Al, and Ca.

Other questions about models for hydrogen storage include (1) What determines the stability of a phase containing hydrogen? (2) Can NAM retain hydrogen to higher temperatures and pressures than the DHMS? (3) What is the role of cation/anion vacancies in accommodating hydrogen in NAM? (4) What is the effect of pressure on the O-H bond? (5) Is hydrogen present in the mantle a product of the original accretion process or was it introduced by comets or meteoritic material and recycled into the mantle over geologic time? (6) If a solid phase containing hydrogen breaks down at high pressures and temperatures of the transition zone, what is the product -- a melt or a fluid or something else?

We do have a relatively good understanding of how hydrogen is incorporated into both the DMHS and NAM. A combination of structure refinement in which hydrogen positions are determined [7] plus simple bond strength calculations [8] provide enough information to establish the immediate environment around hydrogen is several different structures, resulting in insight about which are the most stable and which of the NAM could contain the most hydrogen.

Another kind of model has been proposed for storage of hydrogen in the core, i.e., in iron hydride [9,10]. Although many investigators discount the possibility of significant amounts of hydrogen being present in the core, one should not overlook the discovery that iron hydride appears to be stable to very high pressures and that an iron hydride composition can explain the seismic properties of the core rather well.

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SUBDUCTION OF HYDRATED BASALT OF THE OCEANIC CRUST: IMPLICATIONS FOR RECYCLING OF WATER INTO THE UPPER MANTLE AND CONTINENTAL GROWTH. R.P. Rapp, Center for High Pressure Research (CHiPR) and Mineral Physics Institute, Department of Earth and Space Sciences, State University of New York at Stony Brook, Stony Brook, New York 11794-2100, USA.

Subduction zones are presently the dominant sites on Earth for recycling and mass transfer between the crust and mantle; they feed hydrated basaltic oceanic crust into the upper mantle, where dehydration reactions release aqueous fluids and/or hydrous melts. The loci for fluid and/or melt generation will be determined by the intersection of dehydration reaction boundaries of primary hydrous minerals within the subducted lithosphere with slab geotherms [1]. For metabasalt of the oceanic crust, amphibole is the dominant hydrous mineral. The dehydration melting solidus, vapor-absent melting phase relationships, and amphibole-out phase boundary for a number of natural metabasalts have been determined experimentally [2,], and the pressure-temperature conditions of each of these appear to be dependent on bulk composition. Whether or not the dehydration of amphibole is a fluid-generating or partial melting reaction depends on a number of factors specific to a given subduction zone, such as age and thickness of the subducting oceanic lithosphere, the rate of convergence, and the maturity of the subduction zone [3]. In general, subduction of young, hot oceanic lithosphere will result in partial melting of metabasalt of the oceanic crust within the garnet stability field [4]; these melts are characteristically high-Al_2O_3 trondhjemites, tonalites and dacites [4,5]. The presence of residual garnet during partial melting imparts a distinctive trace element signature (e.g., high La/Yb, high Sr/Y and Cr/Y combined with low Cr and Y contents relative to demonstrably mantle-derived arc magmas). Water in eclogitized, subducted basalt of the oceanic crust is therefore strongly partitioned into melts generated below about 3.5 GPa in "hot" subduction zones. Although phase equilibria experiments relevant to "cold" subduction of hydrated natural basalts are underway in a number of high-pressure laboratories [e.g., 6] , little is known with respect to the stability of more exotic hydrous minerals [e.g., ellenbergite] and the potential for oceanic crust (including metasediments) to transport water deeper into the mantle.

If small amounts of water are available to eclogitized basalt of the oceanic crust at depths in the range 5.0-10.0 GPa, recent experimental results suggest that it will be partitioned into hydrous fluids and/or melts at temperatures between 1000°C-1200°C, rather than in dense, high-pressure hydrous minerals. Based upon a qualitiative assessment of hydrous fluid/melt-eclogite wetting characteristics at these conditions, these fluids/melts will be highly mobile, and will scavenge SiO_2, K_2O, and to a lesser extent TiO_2 from the garnet-clinopyroxene residue. Low-degree partial melts are thus "granitic" in composition. Large-scale melting of hydrated basaltic crust was probably instrumental in establishing the continental crust in the Archean, but as the Earth's thermal regime cooled, this process became less important. Nevertheless, most water within the subducted oceanic crust will eventually enter a hydrous fluid/melt , rather than be transported to great depths via hydrous minerals.

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Surface Ices in the Outer Solar System. Ted L. Roush[1] and Dale P. Cruikshank[2], [1]Dept. of Geosciences, San Francisco State Univ., c/o NASA Ames Res. Ctr., MS 245-3, Moffett Field, CA 94035-1000; [2]NASA Ames Res. Ctr., MS 245-6, Moffett Field, CA 94035-1000

Planetary volatile inventories are products of several factors: (1) condensation-accretion of pre-planetary material which determines the bulk volatile inventory; (2) energy history of a planet, including timing, causes, and mechanisms of degassing; (3) the volatile sinks, including temporary, long term, and permanent; and (4) external processes operating on the volatile inventory. Information regarding the current surface compositions provide insight into both internal and surface-atmosphere evolutionary history.

Our discussion focuses upon the surface composition of outer solar system planets and satellites as determined by spacecraft and telescopic spectral observations. We provide a review and an update of the recent work by Cruikshank and Brown [1] that includes more recent observations and interpretations.

In the context of formation and evolution of solar system bodies, the interesting ices typically considered are simple molecules formed from elements having high cosmic abundances. These mainly include ices of H_2O, NH_3, SO_2, H_2S, CH_4, CO, CO_2, and N_2. In the solid state, these ices have vibrational spectral features, analogous to their gaseous counterparts but rotational transitions are quenched, that lie in the near- and mid-infrared. The overtone and combination modes, occurring in the visible and near-ir region, are of particular importance as standard observational techniques used to identify these ices rely upon reflected solar energy. Table I summarizes the ices found on various bodies in the outer solar system. H_2O is most abundant surface material in the inner and middle regions while more volatile species appear to dominate surfaces in the outermost edge of the outer solar system.

H_2O is the only ice detected with certainty on three large satellites of Jupiter, and all the large satellites of Saturn and Uranus. Despite this geochemical similarity, spacecraft images of these bodies and their different spectral character show them to have diverse geological histories. Internal evolutionary scenarios and bulk densities suggest that H_2O is a major component in the outermost region of the solar system. The apparent dominance of the more volatile surface ices may represent a veneer introduced by exogenous sources such as comets.

N_2 ice is a poor absorber of near-ir radiation, and to detect the absorption near 2.16 μm requires relatively high abundances. Interpretations, based upon modeling of recent high spectral resolution telescopic observations of Triton and Pluto [2,3], suggest that on these bodies N_2 ice comprises $\geq$98 wt.% of the surface ices. Spectroscopic modeling of the N_2 band shape indicates the surface temperature of Triton and Pluto are $\approx$38K and $\approx$40K, respectively [4,5]. The position of the CH_4 ice absorptions of both bodies indicate some of the CH_4 occurs as a solid solution trapped within the N_2 matrix [2,3]. Additional spectral modeling suggests that up to 15% of the surface could be pure CH_4 deposits and still remain consistent with the observations [6]. Residual spectral features seen on the short wavelength side of the 2.35 μm CH_4 ice feature have been suggested to indicate the presence of saturated hydrocarbons [7].

Recent modeling of existing spectral reflectance data for Pluto's moon, Charon, included considerations of both two and three component spatial and intimate mixtures of H_2O, CO_2, and CH_4 ices [8]. Results of this modeling indicates that in addition to H_2O ice, up to 40 wt.% of other icy components may be present on Charon, yet remain undetected [8]. Future observations involving higher spectral resolution and separately resolving the signals from Pluto and Charon are needed to address this issue.

Table I. Surface Ices in the Outer Solar System, from [1]

Jupiter's Satellites	
Io	SO_2, H_2S, (H_2O ?)
Europa	H_2O (NH_3 ?)
Ganymede	H_2O
Callisto	H_2O
Saturn's Satellites	
Mimas	H_2O
Enceladus	H_2O (NH_3 ?)
Tethys	H_2O
Dione	H_2O
Rhea	H_2O
Hyperion	H_2O
Iapetus	H_2O
Rings	H_2O
Uranus' Satellites	
Miranda	H_2O
Ariel	H_2O
Umbriel	H_2O
Titania	H_2O
Oberon	H_2O
Neptune's Satellite	
Triton	N_2, CH_4, CO, CO_2
Pluto	N_2, CH_4, CO
Charon	H_2O

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DEGASSING HISTORY AND EVOLUTION OF VOLCANIC ACTIVITY OF TERRESTRIAL PLANETS BASED ON RADIOGENIC NOBLE GAS DEGASSING MODELS. S. Sasaki and E. Tajika, Geological Institute, School of Science, University of Tokyo, Bunkyo-ku, Tokyo 113 Japan

Current abundances of radiogenic noble gases (4-He, 40-Ar, 129-Xe) in the planetary atmospheres provide valuable information on planetary evolution through their degassing histories. Of these, 40-Ar (from 40-K with half life 1.25Ga) can be used to envisage long-term degassing from the interior. Present amounts of 36 and 40-Ar should have information on timing and degree of degassing from the interior [1, 2]. On the other hand, 129-Xe (from 129-I with half life 17Ma) is used in discussing early planetary degassing [3, 4]. Because life time of helium in the atmosphere is short, atmospheric 4-He (from 235-U, 238-U, 232-Th) data might be used only for current degassing.

The relative abundance of 40-Ar in the Cytherean atmosphere is 0.26 of that in the Earth's atmosphere. We have executed numerical calculation of a 40-Ar degassing model along with mantle evolution and melt migration. Our result shows that the average magma production rate on Venus is about 5 [km^3/yr]. Duration of plate motion on Venus, if existed, would be less than several hundred million years.

For Mars, estimated volume of erupted volcanic materials is compatible with the present Martian 40-Ar, which is about 1/20 of 40-Ar in the Earth's atmosphere. Efficient degassing due to plate tectonics, if existed [5], should have been limited. Difference of 40-Ar abundance normalized to the total solid mass, in the first approximation, should express difference of degree of long-term volcanic activities among planets. On the other hand, degree of the early degassing estimated from Martian radiogenic 129-Xe is as much as 1/3 that of the Earth. We prefer that this early degassing should be due to the magma ocean cooling.

Detection of Martian 4-He will be evidence of current degassing activity on Mars. EUVE observation [6] suggested tentative 4-He abundance in the Martian atmosphere 1.4+-0.4ppm. PLANET-B XUV will provide more precise observation of 4-He. Abundant 4-He in the Venus atmosphere, showing much longer residence time (800Ma) than the Earth's 4-He (1Ma), should correspond to current absence of magnetic field of Venus.

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A CRYSTALLOGRAPHIC MODEL FOR HYDROUS WADSLEYITE (β-Mg_2SiO_4).

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Wadsleyite (β-Mg_2SiO_4) is believed to be the most abundant phase in the Earth between depths of 400 and about 525km. Because of the unusual crytsal chemistry, Smyth [1] suggested that this phase might be a significant host for hydrogen in the transition zone. Indeed, of the nominally anhydrous phases believed to make up the upper mantle and transition zone none has been reported with a greater H content than wadsleyite. Young et al, [2] report the synthesis of hydrous, Fe-bearing wadsleyite with up to 60,000 H per 10^6 Si.

Using ionic constraints and maximal subgroup symmetry, a hypothetical, ordered model for hydrous wadsleyite has been created and examined. The model has formula $Mg_7Si_4O_{14}(OH)_2$, has space group *Pmmb*, has an ordered vacancy into one of two non-equivalent M2 sites, and contains two different H positions, one on each of the non-equivalent O1 sites. Electrostatic calculations indicate that hydration would relieve the underbonding of O1 as well as the overbonding of the bridging oxygen, O2, so that the hydrous phase may be more stable than the anhydrous phase. This model makes several predictions that may be of significance for the mechanisms and amounts of H that may be stored in the transition zone of the Earth, and by which the model may be tested experimentally.

The model predicts that partial hydration of O2 suggested by Downs [3] is very unlikely as it would result in unreasonable distortion of the silicate tetrahedra, whereas full hydration of O1 would decrease distortion of the tetrahedron. The model predicts strong *c*-axis polarization of IR and Raman O-H stretching absorptions. The model predicts that, under hydrous conditions, trivalent octahedral cations Fe^{3+}, Cr^{3+} and Al^{3+} should be more soluble in wadsleyite than in olivine or in spinel (γ-Mg_2SiO_4). Finally the model predicts a maximum H_2O content for the hypothetical phase of 3.3 weight percent. This implies that the transition zone of the mantle might contain several times the amount of H currently in the Earth's hydrosphere if the nominally anhydrous wadsleyite phase were fully hydrated. It further raises the possibility that the amount of surface water on the planet may be buffered by a large internal reservoir and that the volume of the oceans may not have been constant over geologic time.

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Semi-Volatiles at Mercury: Sodium (Na) and Potassium (K). A. Sprague[1]. [1]Lunar and Planetary Laboratory, The University of Arizona, Tucson, AZ 85721.

Several lines of evidence now suggest that Mercury is a planet rich in moderately-volatile elements such as Na and K. Recent mid-infrared spectral observations of Mercury's equatorial and mid-latitude region near 120 degrees mercurian longitude [1] indicate the presence of plagioclase feldspar. Spectra of Mercury's surface exhibit spectral activity similar to labradorite (plagioclase feldspar with $NaAlSi_3O_8$: 30-50%) and bytownite ($NaAlSi_3O_8$: 10-30%). These surface studies were stimulated by the relatively large abundance of Na and K observed in Mercury's atmosphere. An enhanced column of K is observed at the longitudes of Caloris Basin and of the antipodal terrain. Extreme heating at these "hot" longitudes and severe fracturing suffered from the large impact event could lead to enhanced outgassing from surface or subsurface materials [3]. Alternatively, sputtering from a surface enriched in K could be the source of the observed enhancement [2]. Recent microwave measurements of Mercury also give indirect evidence of a mercurian regolith less FeO-rich than the Moon [4]. An anomalously high index of refraction [5] derived from the whole-disk integrated phase curve of Danjon may also be indicative of surface sulfides contributing to a regolith that is moderately volatile-rich. The recent exciting observations of radar-bright spots at high latitudes also indicate that a substance of high volume scattering, like ice, is present in shadowed regions [6]. Other radar-bright spots have been seen at locations of Na enhancements in the atmosphere [7]. All combined, these pieces of evidence point to a planet that is not severely depleted in volatiles or semi-volatiles.

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IMPLICATIONS OF NOBLE GASES IN A RECENTLY RECOGNIZED MARTIAN METEORITE (ALH84001) FOR THE DEGASSING HISTORY OF MARS. T. D. Swindle, Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721 USA.

For terrestrial planets, atmospheric compositions are not static, but evolve with time, in part due to degassing of the interior. Unfortunately, the evolution is slow enough that it is usually not observable on human timescales, or even on the timescales of rocks that preserve samples of Earth's ancient atmosphere. Preliminary results on a recently recognized martian meteorite, ALH84001, indicate that it is a very old rock, and has a relatively high noble gas content suggestive of atmospheric incorporation, but with an isotopic composition slightly inconsistent with currently known martian reservoirs. Hence, this rock may provide a sample of ancient martian atmosphere, which can be used to test models of volatile evolution (in particular, degassing) on Mars.

ALH84001 is a cumulate orthopyroxenite. Although originally classified as a diogenite, its oxygen isotopes, and several chemical and petrographic features, strongly suggest that it is, like the SNC meteorites, martian [1]. A Sm-Nd crystallization age of 4.5 Ga has been reported [2].

The meteorite is rich in noble gases, compared to most SNCs [3,4]. In many respects the noble gases are typical of SNC meteorites. However, there are some subtle differences. In particular, the Xe isotopes in SNC meteorites can be explained as a mixture of martian atmospheric Xe (as represented by glass in EETA 79001), the Xe in the dunite Chassigny (usually assumed to be representative of the martian interior, and with lower $^{129}Xe/^{132}Xe$, $^{134}Xe/^{132}Xe$ and $^{136}Xe/^{132}Xe$ ratios), and later additions from known processes like fission, spallation and terrestrial contamination. The isotopic composition of ALH84001 is inconsistent (at >2-3σ) with any mixture of those components. Even if no accumulation of fission Xe during the age of the rock is assumed, there is too little ^{136}Xe and ^{134}Xe for the amount of ^{129}Xe measured.

Most of the possible explanations for this difference have important implications for models of martian volatile evolution. Assuming that this meteorite really is from Mars, possibilities include:

1) This meteorite samples yet another noble gas reservoir in Mars, in which case Chassigny might not be representative of the martian interior and should not be used in degassing models.

2) This meteorite might have excess ^{129}Xe from the decay of ^{129}I (15.7 Ma halflife). The existence of rocks with live ^{129}I in them early in Mars' history is consistent with one model of the evolution of the I-Xe system on Mars [5]. In principle, this could be directly tested with a standard I-Xe experiment, but Antarctic meteorites typically have extreme iodine contamination.

3) This meteorite might have sampled a less-evolved martian atmosphere. Since ^{129}I has a shorter halflife that the fission Xe progenitors (^{238}U and ^{244}Pu), high $^{129}Xe/^{132}Xe$ ratios might be expected to evolve before high $^{134}Xe/^{132}Xe$ and $^{136}Xe/^{132}Xe$ ratios. There are two problems with this explanation. One is that it is not clear that a rock which has experienced at least two shock events [6] could retain an atmospheric noble gas signature for 4.5 Ga. The other, perhaps more serious, problem is that mathematical models of martian atmospheric Xe using known components and processes do not seem to require (or even permit, in any reasonable fashion) any contribution of fission products to martian atmospheric Xe [7,8].

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WATER ABUNDANCE AND ACCRETION HISTORY OF TERRESTRIAL PLANETS. H. Wänke and G. Dreibus, Max-Planck-Institut für Chemie, Box 3060, D-55020 Mainz, F. R. Germany.

According to a widespread believe, Earth's water was either added in form of a late volatile-rich veneer or as we have argued repeatedly that of all the water which was added to the Earth only that portion remained which was added towards the end of accretion when the mean oxygen fugacity of the accreting material became so high that metallic iron could not exist any longer. Prior to this moment, all the water in the latter scenario would have been used up for the oxidation of iron.

$$Fe + H_2O \rightarrow FeO + H_2$$

Huge quantities of hydrogen would continuously be produced in this scenario which escaped. In the same moment the hydrogen on its way to the surface would lead to an efficient degassing of the growing Earth's mantle. The fact that - assuming C1 abundances - the amount of iridium in the Earth's mantle agrees within a factor of two with the total water inventory of the Earth's mantle and crust is taken as evidence for the validity of such a scenario.

In both scenarios, the Earth's mantle would remain dry and devoid of other volatiles. Some species soluble in metallic iron like carbon and hydrogen will probably partly enter the core in some portions.

It is generally assumed that today a considerable portion of the earth's total water inventory resides in the mantle. It is also clear that over the history of the Earth the water of the Earth's oceans has been recycled many times through the mantle. This is the consequence of plate subduction. In a similar way mantle convection was probably responsible to bring water into the originally dry mantle. As a consequence, today the Earth is wet both inside and outside.

The Earth is the only terrestrial planet having larger quantities of water at its surface. Of the two planets inside the Earth's orbit water seems to have been detected in form of ice on the floors of permanently shaded craters of Mercury. Due to the absence of a noticeable atmosphere the permanently shaded craters provide excellent cold traps. Similar scenarios might be expected on the permanently shaded craters of the Moon. On Venus the atmosphere leads to a even temperature distribution and the only water at the surface of the planet is water vapor in the Venusian atmosphere. The total amount of this water is small. Compared to the Earth's oceans the amount of water in the Venusian atmosphere is about four orders of magnitude smaller.

At present water on Mars is only observed in larger quantities in the North polar cap. The presence of more water in the Martian regolith is under debate. However there is ample evidence of an early period in the history of this planet during which abundant water existed on its surface. From the mass of the material eroded away to form the flood features around Chryse Basin, Carr [1] estimated that at least an amount of water equivalent to an ocean of 44 m averaged over the whole planet is required. Extrapolating the Chryse results to the whole planet, Carr obtained a global inventory of 440 m.

On the contrary, the SNC meteorites as representatives of Martian surface material are extremely dry rocks. In turn the SNC meteorites point to a Martian mantle which contains at least one order of magnitude less water than the Earth's mantle. We should also note that as evident from the oxygen isotopes [2], most of the trace amounts of water found in SNC meteorites is Martian surface water and not mantle derived water. This observation also excludes at least for the more recent history of Mars any larger exchange of water between surface and the interior of this planet.

Thus opposite to the Earth, Mars at least was once wet outside but is dry inside. Carr and Wänke [3] have suggested that this might be the consequence of the absence of plate tectonics on Mars because of which wet surface material was never not yet folded into the interior as it was the case of the Earth.

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He, Xe and Ne ISOTOPES IN A STEADY-STATE MASS TRANSPORT MODEL AND IMPLICATIONS ABOUT TERRESTRIAL VOLATILES. G. J. Wasserburg and D. Porcelli, Lunatic Asylum, California Institute of Technology, Pasadena, CA 91125

We present a model of the steady-state transport assuming three reservoirs: a lower mantle (P) with a relatively undepleted inventory of U, Th, Pu, I, He, Ne, Xe, Ar; an upper mantle that has been extensively outgassed (D); and the atmosphere. There is mass transport at a rate $\dot{M}_{PD}$ by plumes from the lower mantle, a fraction of which is outgassed directly into the atmosphere, while the remainder feeds matter and associated nuclei into D. D is well outgassed at spreading centers and has material containing atmospheric gases added to it by subduction. In the case of He, there is no subduction component. The approach follows the treatment of Kellogg and Wasserburg (1990). A summary of the pertinent equations and constraints was reported earlier (Porcelli and Wasserburg, 1994). The U, Th and Pu in P are estimated for Earth models from refractory element abundances in meteorites. In this model the inventory of rare gases in D is governed by the simple mixing of components from P (both radiogenic and original) with distinctive atmospheric components. In addition, alpha decay and spontaneous fission of U, and (α,n) reaction on oxygen from energetic α particles produce radiogenic/nuclear daughter products in D. These include ^{4}He, ^{136}Xe and ^{21}Ne. ^{40}K in Dgenerates excess radiogenic ^{40}Ar. The production rates in D are a key bridge connecting the various isotopes and the mass transfer rates. The time scale for production of these nuclei is given by the residence time $\bar{\tau} \approx M_D/\dot{M}_{MOR}$ (Kellogg and Wasserburg, 1990) where $\dot{M}_{MOR}$ is the rate for mass processing (of D) to produce MORB. The extensive outgassing of D causes enhanced isotopic shifts in the rare gases in D. The isotopic shifts produced in D are proportional to the nuclear rates times the concentration of the parent nuclei (U, Th, K)and the residence time, and inversely proportional to the concentration of the isotope in D. The relative production rates of ^{4}He, ^{136}Xe, and ^{21}Ne are known nuclear parameters. The absolute production rates in D then depend only on the concentrations of U, Th, and K in D and $\bar{\tau}$. From the U, Th, Pu budget it is found that ^{244}Pu fission dominates the ^{136*}Xe radiogenic component in P while U and Th govern the ^{4}He in P. No independent estimates of ^{129}I are known. We assume that Ne of appropriate composition is also in P as well as ^{3}He. Important discoveries by previous workers have demonstrated the presence of ^{3}He (Clarke *et al.*, 1969; Krylov *et al.*, 1974), ^{129*}Xe and ^{136*}Xe (Butler *et al.*, 1963; Staudacher and Allègre, 1982) reflecting the presence of trapped original gases, ^{129}I decay products, and a fission Xe component. These are recognized by the distinct isotopic composition of these gases relative to the atmosphere. Also, it has been shown that ^{20}Ne/^{22}Ne and ^{21}Ne/^{22}Ne in mantle-derived samples is distinct in isotopic composition from that of the atmosphere (Sarda *et al.*, 1988; Honda *et al.*, 1991; Hiyagon *et al.*, 1992). It has been established that ^{136}Xe/^{130}Xe and ^{129}Xe/^{130}Xe in MORB samples are well correlated and appear to reflect variable additions of atmospheric Xe to a "single" mantle Xe component from a radiogenic source in the mantle. Most commonly Xe in OIB samples exhibit atmospheric compositions, which we interpret as due to contamination in the near-surface environment. We will present the results of the formal model and show that this model is compatible with the observations. The consequences of these arguments are that: 1) there is an average Xe composition in D distinct from the atmosphere. The isotopic composition of Xe, Ne and He in the depleted mantle from which MORBs are derived is the result of mixtures of He, Xe, and Ne resulting from contributions from P (with its own distinctive concentrations and compositions)and from subduction into D of atmospheric Xe, and Ar supplemented by nuclear production in D of ^{4}He, ^{136}Xe and ^{21}Ne. The lower mantle contains Xe with an isotopic composition which is radiogenic and distinct from the atmosphere. 2) The ^{129}I present when the earth formed was ~10^{-4} of the solar abundance in agreement with Wetherill (1975). 3) Only a small fraction of the rare gases in the atmosphere are from the earth's interior. 4) The atmosphere is a late addition, added to the earth after the upper mantle was outgassed (Δt ~100 my). It is possible that this outgassing process and the loss of an early atmosphere, presumably including water, might be related to the impact of a Mars-sized body on the Earth, proposed for the origin of the moon (Cameron and Ward, 1976). The source for the late-added atmosphere is undefined but must respect the issues raised by Hunten *et al.* (1987) and Pepin (1991). Div. Contrib. (859).

Storage and recycling of water and carbon dioxide in the earth. Bernard J. Wood, Department of Geology, University of Bristol, Bristol, BS6 5UE, UK.

The stabilities and properties of water- and carbon-bearing phases in the earth have been determined from phase equilibrium measurements, combined with new data on the equations of state of water, carbon dioxide, carbonates and hydrates. The data have then been used to predict the fate of calcite and hydrous phases in subducting oceanic lithosphere.

From the compositions of MORBs one can estimate concentrations of water and carbon of around 200 ppm and 80 ppm respectively in the upper mantle. Lower mantle estimates are very uncertain, but 1900 ppm water and 2000 ppm C are plausible concentrations.

Measurements of the density of supercritical water to 3 GPa demonstrate that this phase is less compressible than anticipated from the equations of state of Haar et al. (1984) or Saul and Wagner (1989) and is closer to predictions based on molecular dynamics simulations (Brodholt and Wood, 1993) or MRK-type equations of state (Kerrick and Jacobs, 1991). Conversely, fugacity measurements on carbon dioxide to 7 GPa show that this fluid is more compressible than predicted from the MRK equation of state. The results imply that hydrates are relatively more stable and carbonates less stable at pressures >5 GPa than would be predicted from simple extrapolation of the low pressure data. Nevertheless, carbonates remain extremely refractory phases within both the upper and lower mantle.

The stability fields of the dense hydrated magnesium silicates (Phase A, Phase E, etc.) are such that, for the average mantle adiabat, they would be unstable by several hundred degrees in the upper mantle. Thus any water in excess of that tied up in a minor potassic phase must reside in solid solution in the anhydrous minerals olivine, pyroxene and garnet and at higher pressures beta-phase and perovskite. Recent measurements of very high solubilities of water in the beta-phase (Young et al. 1993) places additional constraints on the amount of water present at around the 410 km discontinuity. Solid solution with water tends to stabilise beta-phase to lower pressure and to broaden the phase transition interval between olivine and beta-phase. If we accept that the 410 km discontinuity is due to this phase transition, then, given recent seismological data, the transition interval is only about 10 km or 0.3 GPa. The maximum water content of mantle olivine which would yield a phase interval this narrow is about 200 ppm. In contrast to 'normal' mantle conditions, subduction zones provide environments where hydrated phases can survive to depths beyond the 410 Km discontinuity. Although the thermal structures of subduction zones are very uncertain, both thermal models and geologic observations imply that there is substantial dehydration of the upper part of subducted oceanic crust. Because of the low thermal diffusivity, however, temperatures are much lower 5–10 km below the top of the slab and hydrates remain stable at least into the transition zone. Given recent estimates of magmatic water flux to the exosphere it seems likely that a similar amount (10+14 gm/yr) is being returned to the lower mantle.

Throughout most of the mantle below 100 km depth it appears that a carbon-bearing phase is stable. Due to the interplay between the oxidation states of Fe and C the stable phase depends on the silicate mineralogy (e.g., O'Neill et al.,1993). In the upper mantle carbonate or carbon dioxide

are stable while in the transition zone diamond is the stable phase. Given a lower mantle mineralogy dominated by perovskite and magnesiowustite, magnesium carbonate (magnesite) should be stable below 660 km depth. Both equation of state data and direct experimental observations (Biellmann et al., 1993) indicate that magnesite is stable throughout the lower mantle. In subduction zones, subducting calcite is transformed to magnesite then diamond and finally, in the lower mantle, back to magnesite again. Given the refractory nature of both diamond and the carbonates it seems likely that almost all subducting carbonate which is not physically removed survives into the transition zone or lower mantle. If about 5 x 10+13 gm/yr of C is being added to the exosphere as volcanic gas, then most of this is returned into the deeper mantle as carbonate in subducting oceanic crust (e.g., Staudigel et al., 1989).

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IS XENON ELDEST? K. Zahnle, NASA Ames Research Center, MS 245-3, Moffett Field CA 94035-1000

It is well known that the solubility of noble gases in magmas decreases with increasing atomic weight. Xenon, the weightiest of the stable noble gases, is the least soluble atmospheric gas in magma. It is not unreasonable to suppose that the noble gases should have degassed from (or equilibrated with) a bubbling mantle in order of increasing solubility, such that xenon was the most rapidly degassed and helium the least [1]. The apparent relative ages of the famous radiogenic noble gas isotopes agrees, at least qualitatively, with this premise.

When atmospheric loss processes are assigned their proper place, several long-standing xenonological puzzles become added evidence for xenon's relative antiquity. Xenon, being in the afore-mentioned sense the oldest atmospheric gas, will have been most greatly subject to escape, be it impact-driven or EUV-driven. Nonradiogenic xenon's pronounced isotopic fractionation has already been attributed to escape [2]; why it should be more fractionated than krypton would be assigned to xenon's greater atmospheric age. The small atmospheric inventory of xenon relative to the other nonradiogenic noble gases, known as the "missing xenon" problem, could easily be explained by differential escape [3]. The relatively tiny atmospheric inventories of the radiogenic daughter products of 129 Iodine and 244 Plutonium, both much smaller than would be expected from the inferred abundances of the parents in meteorites, offer a third and fourth data to support the hypothesis that Earth has lost most of its xenon.

The early Earth probably afforded ample opportunity for mantle-atmosphere melt-vapor equilibration. Giant impacts provided one, or more likely, several. A more sustained global melting would have been triggered by the combined energies of accretion and insolation in the presence of a substantial hydrosphere [4]; the result would be a (an episodic) runaway greenhouse atmosphere.

Such a magma-solubility, high escape model is not without difficulties. Aside from requiring hefty xenon losses, which can be difficult to explain when we are already somewhat taxed to explain why the terrestrial planets have so much noble gas, a naive magma-ocean model predicts that the noble gases in the mantle would look like the dissolved complement of the noble gases in the atmosphere. This objection is best answered by another process, e..g. subduction of sediments, that could re-gas the mantle selectively in favor of the more easily adsorbed elements.

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DEGASSING MECHANISMS OF NOBLE GASES FROM CARBONADO DIAMONDS. S. Zashu and H. Hiyagon, Department of Earth & Planetary Physics, University of Tokyo, Tokyo 113, Japan

Diamonds are unique samples for inferring ancient mantle conditions, because of their enormous stability, antiquity and also of mantle origin. However, as temperatures in the mantle where diamonds have existed are very high(> 1000°C) and residence time of some diamonds could be more than a few billion years, it is imperative to examine whether or not diamonds have retained their pristine characteristics, especially those of noble gases, under such extreme conditions.

As discussed in a review article by Ozima[1], there are rather large variations in the diffusivity of helium in diamonds obtained in the early determinations. The data are also limited for temperatures higher than 1200°C. In the present study, we conducted more refined diffusion experiments for He using carbonado diamonds, which have large amounts of radiogenic ^4He($\sim 10^{-2}$ cm^3STP/g)[2]. On the basis of the experimentally estimated diffusion coefficients, we will discuss retentivity of He in diamonds in the mantle condition.

Two carbonado diamonds from Ubangi, Central Africa were studied for helium diffusion by employing incremental stepwise - heating method for temperature ranges from 350 to 1800°C. Diffusion coefficients D were calculated for each temperature step using the standard approximation of equi-sized spherical grains with initially homogeneous helium concentration. Arrhenius plots of the experimental data demonstrate that there exist two degassing mechanisms of helium from diamond; the lower temperature degassing(T < 1500°C) is most likely volume diffusion and the higher temperature degassing(T > 1500°C) is essentially governed by graphitization of diamond. Diffusivity calculated from the observed release rates of the lower temperature range defines Arrhenius relations with an activation energy of 103.5 ± 4.8 kJ $mole^{-1}$ and a pre-exponential factor, $D_0 = 10^{-13.2 \pm 0.2}$ cm^2 sec^{-1} in carbonado diamond. Using these values, we can estimate the diffusion coefficient of He to be 3 x 10^{-17} cm^2 sec^{-1} at 1300°C.

We assume the present results can also be applicable to He diffusion in common diamonds and evaluate retentivity of He in diamonds in the mantle condition. We can calculate a characteristic diffusion length of He to be about 2 cm in 4.5 x 10^9 y. This value is rather small in considering the extreme condition we assumed, indicating high retentivity of He in diamonds. However, the diffusion length is still too large for diamond to retain He in such an extreme condition as in the upper mantle for the whole history of the earth. For the following reasons, however, we must point out here that there still remains a possibility that the diffusion coefficients of He obtained in the present study may be overestimated. Since carbonados are aggregates of diamond microcrystals, the effective grain size might be smaller than those estimated in the present study for calculating the diffusion coefficients. Moreover, implantation of ^4He emitted from U and Th into carbonados might have caused some radiation damages in the crystals. This would result in faster loss of ^4He from the samples, and hence result in overestimation of the diffusion coefficients. If these are the cases, retentivity of He in diamonds may be even higher than that estimated above.

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